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Modern Coal Pyrolysis

A State-of-the-art Review

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PREFACE

During 1979, coal research became a major activity of the Alberta Research Council, particularly studies into conversion of coal to liquid products, the recovery by underground gasification and the geology of Alberta deposits.

In January 1980, the Research Council completed a detailed five-year Coal Research Program on liquefaction, pyrolysis (partial liquefaction), underground gasification and supporting studies. This report "Modern Coal Pyrolysis: A State-of-the-art Review" forms part of Phase I of the pyrolysis program. Part II involves building and operating a versatile bench unit for evaluating local subbituminous coals and the products obtained from different pyrolysis conditions.

Although initially intended as background for the Research Council's program only, the present study should also provide useful information to engineers and scientists engaged in various aspects of coal research and development and technology assessment. Consequently it was decided to issue the study as an Information Series Report.

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SUMMARY

This report forms part of Pyrolysis Program: Phase I, of the Alberta Research Council's Coal Research Department. It summarizes relevant information from the open literature on the chemistry of coal pyrolysis and its application to process development. Available data on known processes are presented and discussed to identify the following: (i) the types of coals tested and the products obtainable; (ii) scales of operation, process flowsheets and equipment details; (iii) operating conditions; and (iv) costs and current development status.

All flash pyrolysis processes involve rapid heating of pulverized coal to between 600° and 900°C. Active decomposition into "tars" and gases occurs in fractions of a second. Secondary hydrocracking reactions increase the gas yields. The amount of volatiles formed exceeds the analytically determined volatile content of the coal. Yields and product composition are critically dependent on coal type and operating conditions. Most of the available test data stem from testing of high volatile bituminous coals which produce high liquid yields.

To date subbituminous coals have received relatively little attention so that reliable predictions of product yields and compositions for particular coals cannot be made. Such forecasting can only come from further bench unit tests.

Comparing assay data of American coals with data of Alberta subbituminous coals indicates that both flash pyrolysis and hydropyrolysis processes could be expected to yield 0.8 to 1.5 bbl of refinable liquids and 4000 scf medium Btu gas per ton of daf coal. Flash pyrolysis processes, operating at moderate pressures, such as the Lurgi-Ruhrgas and Occidental (Garrett), are further advanced technically than flash hydropyrolysis processes: they produce low temperature tar that can be hydrogenated to refinable liquids, but their high solids circulation rates and large equipment sizes result in relatively high capital and operating costs. Flash hydropyrolysis processes operating under high pressure with short residence time reactors have potential advantages of higher liquid yields and lower costs, but are still at an early stage of development. Exploratory tests with Alberta subbituminous coals in the Cities Service flash hydropyrolysis bench unit gave oil yields ranging from 14 to 20 percent of coal feed with 60 percent overall conversion to gases and oil. The benzene, toluene and xylene content of the oil was 50 percent (private communication). Reactivity of char to combustion and gasification has not been determined.

Apparently the current state-of-the-art in flash pyrolysis does not permit either selection of process routes best suited to different coal types or prediction of product yields and quality for specific coals. Performance predictions for Alberta coals cannot be based on recent American research and development programs where the main objective has been to develop pyrolysis processes emphasizing syngas production from high-sulfur bituminous coals.

The main development work in catalytic hydropyrolysis processes is based on the competitiveness with the slurry-phase liquefaction of U.S. high-sulfur bituminous

coals. Limited studies carried out in bench-scale operation have indicated that higher oxygen contents in the feed coals is deleterious to ultimate conversion, and gas yield dominates over liquid yield.

The Cities Service-Rocketdyne process is conceptually attractive for Alberta conditions. It aims for 50 percent conversion in the short residence time flash hydropyrolysis reactor, coupled with char utilization by either gasification for hydrogen generation or combustion for electric power generation. At this stage, however, little is known about reaction parameters controlling the conversion of Alberta coals for optimum liquid yield, about char and liquid properties, or about the effect of catalysts on product qualities, and yields.

The reactor concept advanced by the Occidental Research Corporation (Garrett Process) merits consideration. It is a combined process technology in which the liquid tarry hydrocarbons are extracted by flash pyrolysis of raw coal, and the resulting char and product gas are used as fuel in a conventional utility boiler. Though the tar yields obtained at the Occidental reactor were twice those estimated for the same coals by Fischer assay testing or by fluidized bed pyrolysis processes with long residence time, the initial product development units tar yield results were low compared to the projections from a bench-scale reactor. Tar cracking occurred on the reactive surface of the recycle char used as heat transfer-agent. For optimization of liquid yields, the reactivity of the heat carrier has to be identified.

This report concludes that extensive bench unit tests will be required to provide data before technical and economic studies can fully evaluate the potential for pyrolysis processes at site-specific locations in Alberta. Processes emphasizing production of synthetic fuels and chemical feed stock are likely to be the most attractive for Alberta.

INTRODUCTION

Coal pyrolysis in fixed beds has had a long history in the production of such things as metallurgical coke and smokeless fuel. The tar and oil by-products have received little attention. More recent investigations have led to the concept of hydrocarbonization, in which the production of coal liquids becomes the primary objective. Currently, process development activities are being carried out by organizations such as Cities Service Limited, Occidental Petroleum Corporation, Institute of Gas Technology, The City University of New York, Pittsburgh Energy Technology Center, the Brookhaven National Laboratory, Oak Ridge National Laboratory and IEA Coal Research. The most significant development is the successful performance of the Rocketdyne reactor. In this 4 inch diameter reactor (1 ton/hr), flash heating of a dilute-phase mixture of coal and hydrogen at high temperature gives a carbon conversion of about 36 percent to liquid products of high benzene-toluene-xylene content and 20 to 30 percent to gas with high methane content.

The development of techniques involving entrainment and/or fluidization of the coal particles during carbonization has made several pyrolysis processes more attractive economically. In such techniques, heat transfer rates are materially increased to give greater throughput and hence lower capital and operating costs for a given size of plant.

This review is intended to assemble in concise format the relevant information available from open literature on the chemistry of coal pyrolysis and its application to process developments. Processes currently in the development stages are considered to identify the following: (i) what product slate each process will generate; (ii) what types of reactors and equipment are to be employed; (iii) the details of reaction parameters and test data to meet the objectives of each process; (iv) and the cost and the current status of each.

This review also intends to evaluate the developing processes for their potential applications in Alberta under a coal technology development program.

PHENOMENOLOGICAL CHEMISTRY

Yields and the characteristics of pyrolysis products are significantly affected by coal properties and pyrolysis conditions. In the laboratory, a coal can be evaluated for its pyrolytic properties by a quantitative "destructive distillation" procedure. Several such assay methods have been standardized to furnish results that can be directly correlated with industrial practices. The Fischer assay, originated in Germany, and the Gray-King assay, originated in Britain, are extensively used for classifying coals.* The liquid product yields from fixed bed pyrolysis generally corresponds to the assay results.

The following generalized sequence occurs during the destructive distillation of coal particles:

100 - 150°C absorbed water is released;

150 - 300°C occluded gases are released;

270 - 300°C finely divided pyrite particles react with organic matter of coal with evolution of hydrogen sulfide;

300 - 350°C all maceral groups start to decompose into a semi-coke and into "proto-bitumen" which starts to boil out of the particle;

350 - 450°C a slow endothermic process occurs with escape of vapors; gases such as hydrogen, methane, carbon monoxide, carbon dioxide and other hydrocarbons are given off; a temperature differential between the outer and inner portion of the grain is established;

450 - 600°C cracking of "proto-bitumen" into gases, lighter hydrocarbons, heavier tar, and carbon residue takes place in and around every grain; the char residue further release gas (mainly hydrogen) until a stable carbon skeleton is left.

The type and nature of coke residue varies according to the maceral distribution*. The cokes from exinite and vitrinite are swollen and foamy. Exinite produces less coke residue than vitrinite, while fusinite produces the largest amount of coke residue and a considerable amount of gas as well. Inertinites do not show any major change other than an increase in the reflectance values. Cracking of vapors is not only dependent on the temperature of the particle but also on the time of heat exposures. The heavy phenolic and asphaltenic "proto-bitumen" seems to be much less stable than the paraffinic vapors from the exinites.

One may conclude from Figure 1 that the yield of pyrolysis products for reasonably long experimental times becomes independent of temperature above 1000°C, but recent data (Blair *et al.*, 1977; Kobayashi, 1976; Ubhayaker *et al.*, 1977) suggest that by heating coal to a temperature well

*Both assays are usually conducted at 500 or 600°C. At such temperatures the results tend to show maximum tar plus "light oil" yield but underestimate gas volumes. The Gray-King assay can also be carried out at 900°C and provides information about the quality of solid residue and maximum gas yield. In the hands of experienced operators both assays are sufficiently precise to yield mass balance of 100 ± 0.3 percent.

* Macerals are banded components of coals recognizable by microscopic examination. They are characterized by their appearance, chemical composition and optical properties, and, in most cases, can be traced back to specific components of the vegetation from which the coal formed.

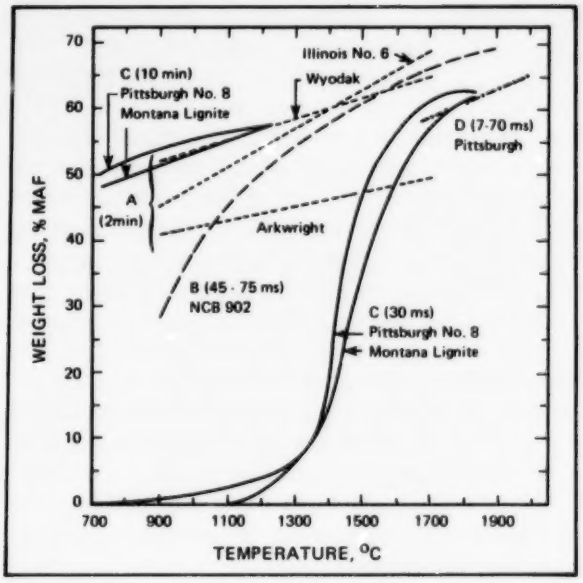

FIGURE 1. Effect of Temperature beyond 1000°C on pyrolysis volatile yield at different residence times (Howard, 1981).

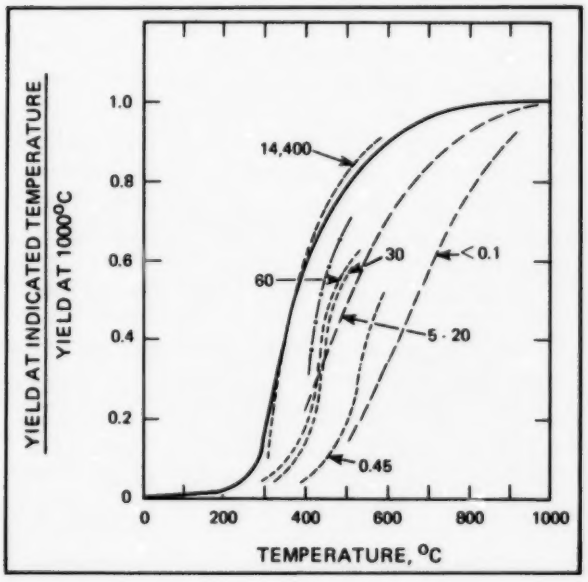

FIGURE 2. Effect of Temperature on pyrolysis volatile yield at different residence times (Howard, 1981).

beyond 1000°C in relatively short times, an additional devolatilization could be affected. This is shown in Figure 2, which suggests that the absolute time required for a given degree of completion of devolatilization is much less when the particle temperature is raised very rapidly. The effective rate of escape of volatiles from the particle at a lower temperature rate may be too slow to prevent secondary cracking and deposition of carbon.

Anthony et al. (1975) found that heating rate per se is not important with respect to volatile yield but does have a clear effect on the temperature-time history of pyrolysis. For example, it was shown that the temperature attained before devolatilization reaches 10 percent completion was 400°C at a heating rate of 1°C/sec, and 840°C at 100 000°C/sec. This effect of the heating rate can clearly influence the nature of pyrolysis products by influencing the partial pressure of the ambient gas at, or within, a particle undergoing decomposition or devolatilization.

The effective volatile content of a coal must be carefully distinguished from volatile matter (VM) determined by proximate analysis. The volatiles escaping from particles in the packed bed employed in proximate analysis undergo secondary reactions including cracking and carbon deposition on the solid surfaces. The total yield of volatiles from pulverized coal dispersed in a gas can be 30 to 40 percent larger than proximate analysis. The tendency to exceed VM is stronger for the intermediate rank hvb coals where the yield of tar also exhibits a maximum. The volatile yield is directly related to the time-temperature history of pyrolysis. This is illustrated in Figure 1, compiled by Howard from data by Dryden (1957), Shapatina (1960), Wiser (1967) and Anthony (1975). The data of each researcher was normalized to 100 percent yield at 1000°C. Dryden's correlation is based on slow carbonization, comparable to those of proximate analysis, of a large number of American and British coals having 30 to 40 percent moisture and ash-free VM. Shapatina's experimental technique was different: coal particles were dropped into a heated chamber with mini-

mum residence time of 0.45 sec, then caught and soaked in a heated trap for the duration of the run. The yields obtained by Anthony with very rapid heating (10 000°C/sec) showed a trend similar to the yields reported by Shapatina at 0.45 sec.

Recent experimental data published by Finn, Fynes, Ladner and Newman (1980), based on a British hvB-b coal (NCB coal rank No. 802; C 82.4 percent, H 5.3 percent) indicate that under flash pyrolytic conditions, low molecular weight compounds are formed by secondary cracking reactions of "proto-bitumen." The yield of BTX (benzene, toluene and xylenes) increases with vapor residence time and is not affected by heating rate; but PCX (phenol, cresol and xylenols) yields reach a maximum at 3 sec vapor residence time and disappear at 8 sec residency, and the evolution time peak becomes narrow with higher heating rate. The BTX yield is not sensitive to pressure but methane yield increases rectilinearly with pressure.

Extensive data published by researchers from MIT, Cambridge, Massachusetts (J.B. Howard and students, 1980) indicate that the cracking reaction is dominant even under hydropyrolysis conditions and is responsible for a complex situation involving simultaneous chemical and mass transfer phenomena. Most of their studies, however, are based on either lignites or hvb-coals and say nothing about subbituminous coals.

Coals vary widely in properties and their behavior under the action of heat is not always predictable. In the case of a material undergoing thermal decomposition, the term "heat capacity" loses its conventional significance and includes heat quantities such as sensible heat, reactions heat or heat of decomposition. Kirov and Stephens of Australia (1967) developed a procedure to measure the enthalpy variation at temperatures ranging from 250 to 500°C and specific heats of coal in "decomposing" and "inert" states up to 900°C using apparatus with a fluidized bed incorporated in an adiabatic calorimeter. They observed that the specific heats of bituminous coals (%C = 80-90, daf) in their inert or non-decomposing states vary from 0.38 cal/g for low hydrogen coal to 0.65 cal/g for high hydrogen coal. The specific heats at "decomposition" states are always high. An intermediate step in determining active and inert specific heats involves the experimental investigation of the heat transfer factor, which varies both with temperature and with stages of decomposing or inert states of coal. They were able to compute, however, the total heats required for coking coals of 20, 30 and 40 percent daf volatile content over a temperature range of 500° to 1000°C (Table 1).

Data of this type are not available for subbituminous coals. Though various attempts have been made to determine the kinetics of decomposition reaction (especially of coking coals) with

TABLE 1.
Estimated total heat of coking from 20°C to t°C in cal/g

Coal:								
	Volatile Matter	% daf			20-40			
	Moisture	%			5-10			
	Ash	%			5-10			
Temperature Range 20°C to			500	600	700	800	900	1000
Total heat of coking, cal/g			225	254	281	312	340	368

Average range: $Q = 82 + 0.286\ (t^{\circ}C)$ cal/g $\pm$ 7%

Data source: Kirov and Stephens (1967)

the help of thermogravimetric analysis, the results are inconclusive. Assuming that the reaction has an order, "that order varied with the progress of the reactions, being some 40 percent lower at the end than at the beginning and it also varied with temperature, e.g. 0.7 at 380°C to 1.8 at 460°C" (Kirov and Stephens, 1967). The pyrolytic reactions of coals appear to be extremely complex.

TYPES OF COALS AND PYROLYSIS

The rank of coals is not a parameter by which the pyrolytic behavior can be predicted. Maceral compositions play a major role. Typical properties of pure macerals of identical rank are given in Table 2.

Exinite (sporinite from spores and pollen, cutinite from waxy plant and leaf cuticles, alginite from algae, and resinite from resins) is rich in hydrogen, low in oxygen, and has carbon similar to or slightly lower than the whole coal of the same rank. Its tar yield is around 40 to 50 percent and decreases rapidly on oxidation. The vitrinite group, whose elemental analyses correspond to that of whole coal of the same rank, melts during early stages of

TABLE 2.
Typical properties of pure macerals of the same rank

Properties	Exinites	Vitrinites	Inertinites	
			Fusinites	Other
% Carbon	82.0 - 83.0	83.0	94.0	83.0 - 85.0
% Hydrogen	8.7 - 9.0	5.5	2.8	2.7 - 5.0
% Oxygen	6.0 - 7.3	9.0 - 10.1	2.3	8.0 - 12.0
% Nitrogen	0.5 - 1.4	1.3 - 2.0	0.9	1.3 - 1.9
% Sulphur	0.5 - 0.6	0.5	-	0.5
Reflectance (oil)	0.2	0.8	3.5+	2.2 - 2.5
% Volatiles	80.0	38.0 - 48.0	5.0	10.0 - 15.0
Fischer Assay				
Oil yield (25%)	40.0 - 50.0	11.0 - 14.0	0	1.0 - 4.0

TABLE 3.
Properties and oil yields from Australian coals

H/C	Rank, % C, daf	Tar + light oil g/100 g Carbon	Maceral distribution %		
			Vitrinite	Exinite	Inertinite
0.994	79.1	31.2	-	-	-
0.886	82.0	16.3	75	4	11
0.816	81.8	12.6	-	-	-
0.807	67.9	10.5	-	-	-
0.775	83.0	16.9	52	11	34
0.736	82.5	9.9	37	8	53
0.682	71.5	0.1	-	-	-
0.646	88.5	6.2	-	-	-
0.576	89.0	0.2	-	-	-

Data Source: Schafer and Tyler, C.S.I.R.O. Australia (1980)

carbonization (380 to 450°C), and produces 12 to 14 percent tar. The inertinite group (fusinite, micrinite, semifusinite, sclereotinite and oxidized resin) has less hydrogen and more carbon than the corresponding whole coal or vitrinite; its tar yield varies from 0 to 4 percent.

The relationship between maceral compositions and oil yields are exemplified by the data given in Tables 3 and 4. It is well established that the higher the hydrogen content of the coal the higher is the oil yield. Perhydrous high volatile coals of bituminous rank give the maximum yields of liquid on pyrolysis. The data on European, African and Australian coals provide the following generalizations:

- good oil yields result from a high percentage concentration of the exinite group of macerals in coal;
- vitrinite in high concentrations also contributes to the oil yield but produces strongly phenolic oils;

TABLE 4.

Properties of European and African coals with Fischer oil yield

Maceral & Mineral	South African Banded coal B-mine	South African Dull coal C-mine	South African Banded coal D-mine	Ruhr	Saar Lorraine	Poland
Exinite	9.0	4.0	1.0	9.4	11.0	low
Vitrinite	51.0	26.0	43.0	70.0	74.5	-
Inertinite	26.0	51.0	47.0	14.0	7.5	-
Mineral	14.0	19.0	9.0	6.6	7.0	12.0
Composition MMF basis						
C%	82.5	84.6	87.0	80.4	83.4	84.2
H%	5.1	4.8	4.8	5.4	5.7	5.1
N%	1.8	1.5	1.2	1.4	1.1	1.4
S%	0.6	0.5	0.6	0.6	0.6	0.7
O%	10.0	8.6	6.4	12.2	9.2	8.5
Oil yields (Fischer)	14.0	7.4	9.4	13.2	14.6	11.0
Vol matters	38.3	26.0	27.2	40.1	36.7	34.1
Slow pyrolysis results from pilot plant						
Total liquids	14.7	-	-	12.8	11.4	10.7
Composition of liquids (vol %)						
C_3-C_4	2.8			3.1	8.0	7.0
C_5-200°	24.8			16.2	16.0	12.3
200-360°C	37.6			51.4	61.0	48.2
Vacuum oil	31.7			14.8		
Vacuum resid	13.1			14.5	15.0	25.8
Phenols	25.0			29.1	32.0	41.5
Bases	1.2			1.3	1.0	n.d.
Waxes	1.0			1.0	n.d.	2.5
Aromatics (in light oil)	36.0			40.0	60.0	42.0

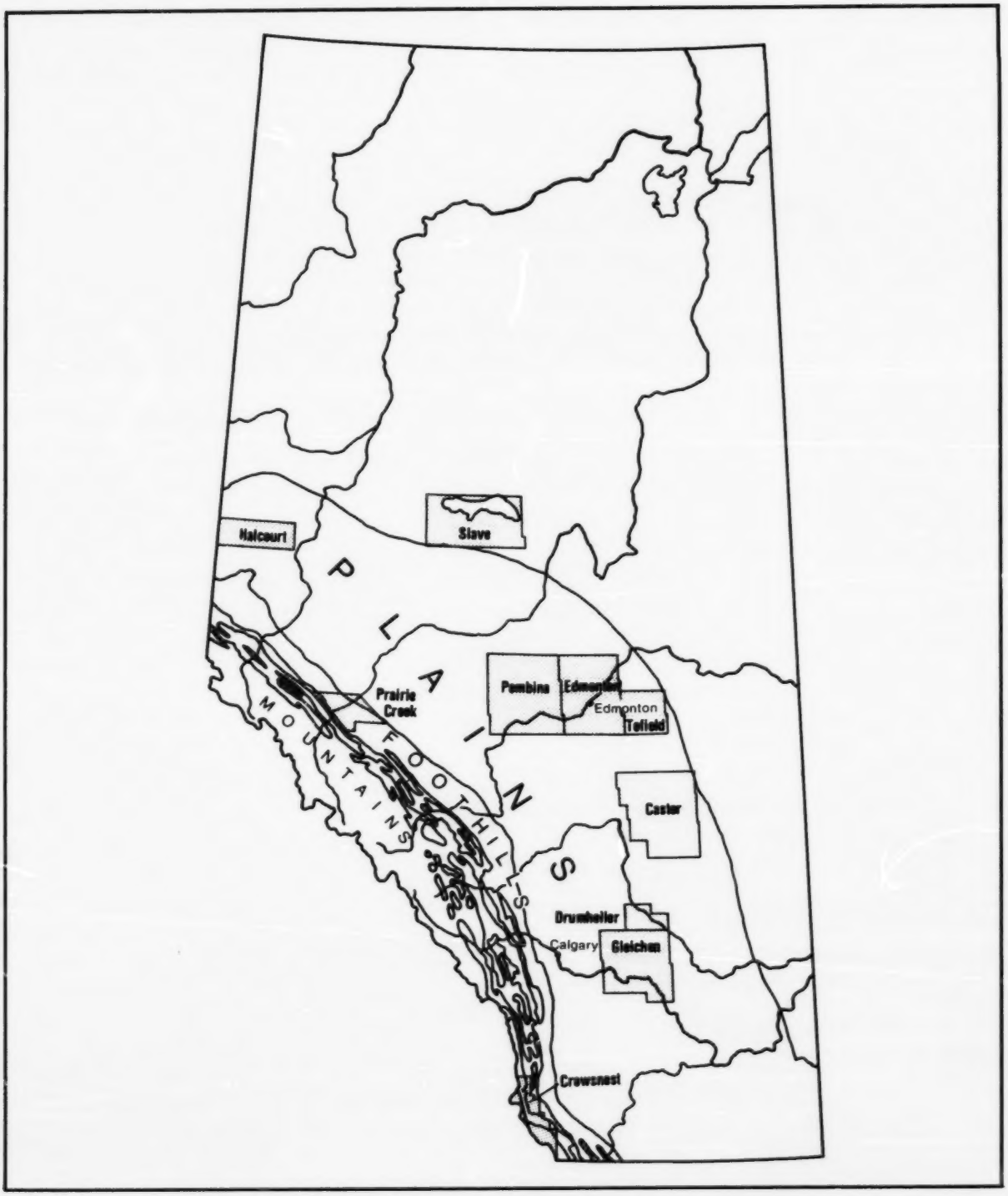

FIGURE 3. Approximate locations of sampling areas for Gray-King assay.

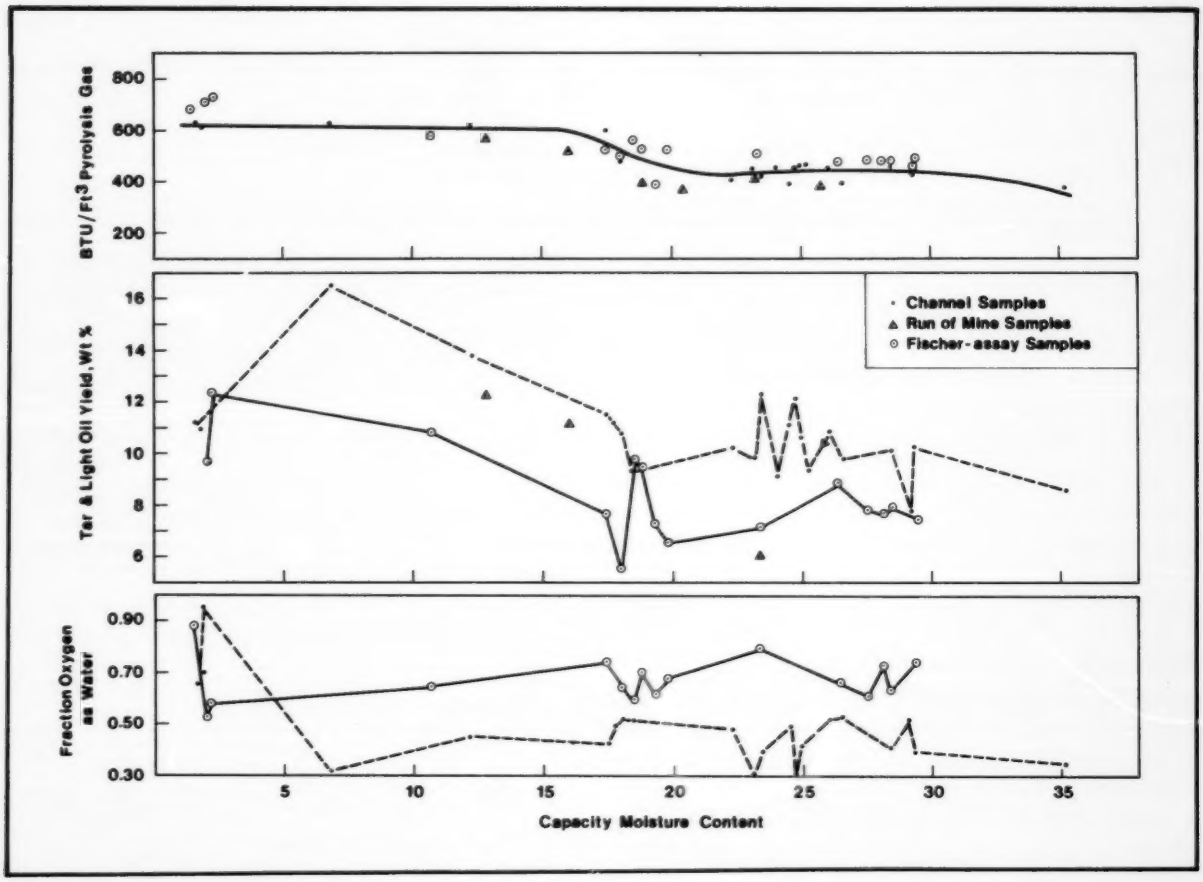

FIGURE 4. Carbonization assay yield vs rank of coals defined by capacity moisture.

- dull coals with a low concentration of exinite (and little vitrinite), known as "gray durain " are unsuitable for oil production by low temperature pyrolysis;
- dull coals with high concentration of exinite, known as "black durain," give very rich oil yield. The hydrogen content of this type of coal generally exceeds 5.2 percent.

COALS OF ALBERTA

Alberta coals date from the Cretaceous period, and differ from carboniferous coals of eastern United States, Europe and the southern hemisphere with respect to thermal and solyvolytic properites. Their maceral compositions are ill-defined and have not been studied extensively. There are two distinct types of deposits of subbituminous rank in the Plains, and coals of medium and low volatile bituminous rank in the Rocky Mountains and Foothills. In the Plains, the subbituminous coals class, having carbon contents of 74 to 79 percent and hydrogen contents of 4.7 to 5.2 percent, constitutes the major reserve.

A survey of the pyrolytic behavior of Plains subbituminous coals was undertaken by the Alberta Research Council in 1948-50 including a Gray-King assay of a few limited samples (Table 5). The data show a spread of tar and gas yield within a given rank as large as 20 percent (Figure 4),

TABLE 5.
Gray-King Assay: Tar and gas yield (as mined coal basis) Alberta coals

Coal District	Tar yield		Gas yield		Data Source
	m^3/ton	bbl/ton	scf/ton (15°C, 101.3 kPa)	m^3/ton	
Slave	0.0652	0.41	4301	0.1212	ARC files
Camrose	0.0638	0.40	3464	0.0975	"
Tofield	0.0662	0.42	3310	0.0933	"
Castor	0.0797	0.50	3568	0.0933	"
Edmonton	0.0726	0.46	3152	0.0888	"
Keephill Highvale mine	0.110	0.63			Projected data by by I.W. Herring. Master Thesis U of Calgary
Gleichen	0.0862	0.54	3207	0.0903	ARC files
Drumheller	0.0886	0.56	3382	0.0953	"
Pembina	0.0740	0.47	3288	0.0926	"
Halcourt	0.0995	0.63	2920	0.0822	"
Prairie Creek	0.103	0.65	2510	0.0707	"
Crowsnest	0.0900	0.57	2812	0.0793	"

presumably because of unidentified differences in maceral compositions. Samples from Drumheller, Halcourt and Prairie Creek deposits gave the highest tar and gas yields, as well as gas with reasonably high calorific values. It is reasonable to assume that variations in capacity moisture content, carbonization assay values and calorific values of pyrolitic gas reflect wide variations in structural make-up of subbituminous coals of the Province of Alberta.

FLASH PYROLYSIS* AND HYDROCARBONIZATION

Berkowitz (1979) described the phenomenon of flash pyrolysis in the following way:

> "When coal is flashed to active decomposition, i.e. heated to 450°C in a fraction of a second...its component molecules tend to fragment more extensively than otherwise; and if the resultant radical species are promptly stabilized and prevented from recombination, the quantities of material then volatilized can exceed the analytically determined volatile matter content of the coal by a wide margin."

Apparently, only vitrinite is sensitive to the speed of heating. Hydrogen distribution (in terms of hydrocarbons rather than elemental hydrogen), after pyrolysis, shows an improvement by fast heating of vitrinitic coals. The oil obtained is much heavier. Table 6 (Taupitz, 1976) comprises slow and fast pyrolysis with regard to products.

The following techniques have been used to accomplish flash pyrolysis:

1. passing gas-entrained coal through a preheated pressurized tube reactor;
2. rapid cycling of gas fluidized coal bed;
3. variants of the above two techniques.

*In current terminology, "flash hydropyrolysis" denotes pyrolysis reactions in the presence of hydrogen.

TABLE 6.
Comparative data of slow and fast pyrolysis

Coal Parameters	South African Coal			Ruhr Coal			Polish Coal	
	Slow	Fast Fluid. Bed	Press. Gasifier	Slow	Fast Fluid. Bed	Press. Gasif.	Slow	Fluid Bed
Oil-yield (compared to assay data)	90-100	100-120	73	100	163	76	95	147%
Composition of liquid, vol%								
C_3-C_4	2.8	-	7.8	3.1	5.0	-	7.0	2.8
C_5 - 200°C	24.8	-	8.7	16.2	14.9	-	12.3	7.2
200 - 360°C	37.6	45	36.0	51.4	15.0	-	48.2	55.0
vacuum oil	21.7	55	-	14.8	24.1	-	-	-
vacuum resid	13.1	-	47.5	14.5	41.0	-	25.8	35.0

Data Source: K.C. Taupitz, Hydrocarbon Processing, November (1976)

A simplified flow diagram is shown in Figure 5. The phenomenon can be assumed to proceed in two quite discrete steps, first forming "proto-bitumen," then hydrocracking this tar-like primary product in the vapor phase to produce gas, light oils, heavy oils and a solid residue. It has been observed that oil yields can be substantially enhanced by pyrolyzing the coal after impregnating it with cracking catalyst (zinc or stannous chloride) or hydroliquefaction catalyst (molybdenum sulfide). Thus the process may be described as catalytic or non-catalytic hydrocarbonization. Maximum oil yields generally result from hydropyrolysis - near 550°C and increase linearly with hydrogen pressure. The presence of a catalyst improves the quality of oil, generating more light fractions, but the effect of catalysts diminished quickly when the temperatures are raised beyond 600°C.

Yields and product compositions from flash-pyrolysis reactions are critically influenced by rank and type of coal, as mentioned above. They also are influenced by process parameters, particularly the geometry of the reactor and operating conditions.

EMPIRICAL CORRELATION

Correlations between the operating conditions and product yields have been deduced empirically for several processes. Some of these correlations are given below. It will be seen that, of all the variables, temperature and pressure are the most important. The residence time of solid materials may have statistical significance in specific processes only.

(a) U.S. BUREAU OF MINES

The U.S. Bureau of Mines hydropyrolysis study (Clarke, 1950; Hiteshue, 1961) was conducted in a batch reactor. The entire charge remained in the vessel for the duration of the experiment and the bed configuration varied from packed to fluidized state depending on gas velocities. The following correlation is based on Rock Spring (Wyoming) bituminous coal processed with temperatures varying from 500 to 600°C, with pressures between 0 and 1000 psi and with hydrogen flow between 0.123 and 20.0 scf/min:

Yield of Products (% daf coal-feed)

$$\text{Oil} = 2.227\, T^{1/2} + 0.5960\, P^{1/2} - 45.189$$

$$\text{Gas} = 1.572 \times 10^{-4} \times P + 0.0319\,T - 0.0764\,P + 0.094\,\theta - 15.014$$

(where θ is solid residence time)

$$\text{Char} = 167.201 - 0.1524\,T - 1.10166\,P^{1/2}$$

Under the COED project, the agglomerating Elkol coal from Wyoming was tested in a similar batch reactor. The experiments covered a temperature range of 411 to 588°C and a hydrogen pressure range of 0 to 5000 psi. The correlation equations are given below.

Yield of Products (% daf coal-feed)

$$\text{Oil} = 4.714\,T^{1/2} + 0.11173\,P^{1/2} - 98.650$$

$$\text{Gas} = 5.3079 \times 10^{-6}\,T \times P + 0.1145\,T - 43.1306$$

$$\text{Char} = 314.185 - 10.39991\,T - 0.31658\,P^{1/2}$$

(b) OAK RIDGE NATIONAL LABORATORY

The authors (Holmes et al., 1975) reported that, for subbituminous and brown coal or lignite, hydrogen consumption under hydropyrolysis conditions varies according to the following equation:

$$\frac{\text{weight of hydrogen consumed}}{\text{weight of daf coal}} \times 100\%$$

$$= 3.1089 \times 10^{-6}\,T \times P - 0.2066\,P + 0.39356\,P^{1/2} + 0.4492\,\theta - 5.481$$

(where θ is solid residence time).

The amount of hydrogen consumed was relatively insensitive to the hydrogen partial pressure in the temperature range of 500 to 600°C, but, at higher

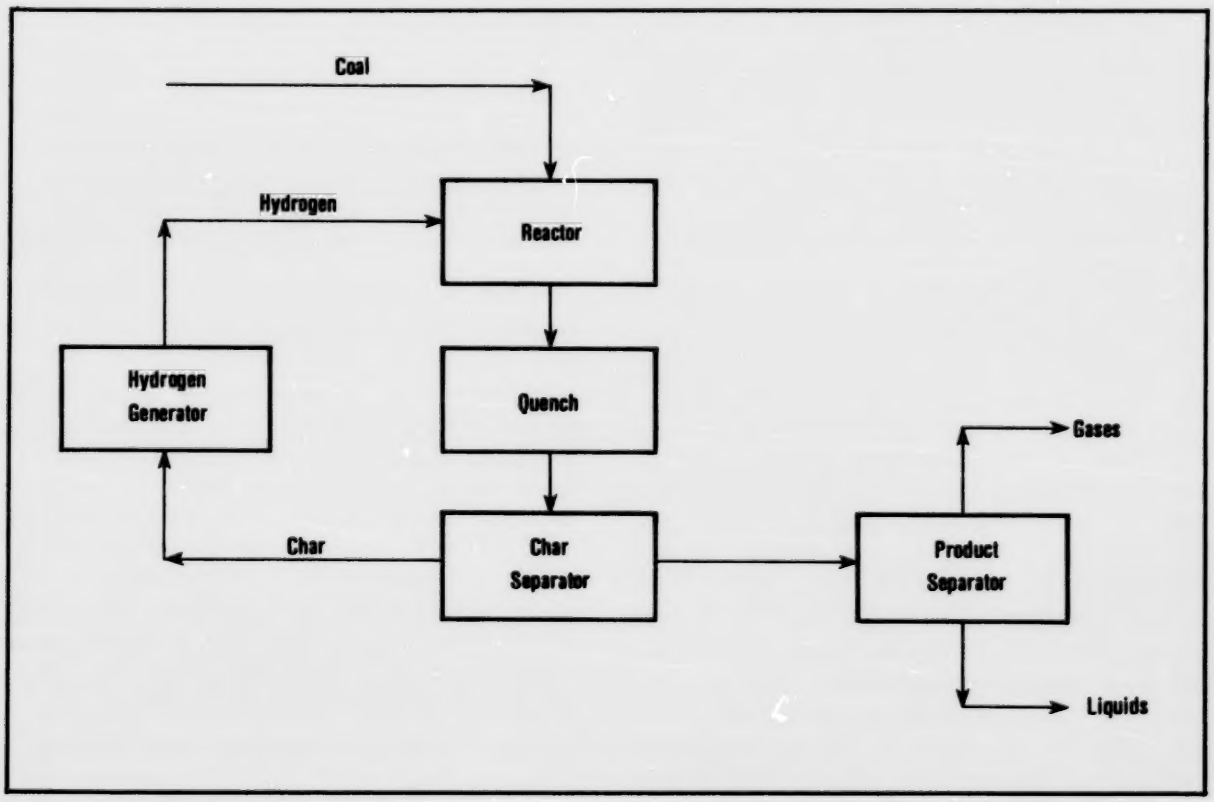

FIGURE 5. Simplified flow diagram of Flash Pyrolysis process

temperatures, increased rapidly with the hydrogen partial pressure. The crossover pressure (corresponding to zero hydrogen consumption) varied approximately between 300 psi at 500°C and 100 psi at 900°C. The empirical correlation cannot be reliably extrapolated and is limited to allowable pressure range as a function of temperature, i.e. 480 to 600°C at 200 to 1000 psi, 700 to 760°C at 150 to 650 psi, 840 to 860°C at 350 to 550 psi, respectively.

(c) UNION CARBIDE CORPORATION

In a bench-scale (1 lb/hr capacity) fluidized bed reactor, hydropyrolysis (Albright and Davis, 1970) of a subbituminous Wyoming coal in a hydrogen atmosphere at 478 to 576°C and 0 to 950 psi hydrogen pressure gave rise to the following empirical relations:

Yield of Product (% daf coal-feed)

$$\text{Oil} = 2.089\,T - 0.001906\,T^2 + 0.01683\,P - 559.179$$
$$\text{Gas} = 1.7117 \times 10^{-5}\,T \times P - 10.8642$$
$$\text{Char} = 253.032 - 0.0168\,T^{1/2} - 0.8874\,P^{1/2}$$
$$\text{Water} = 3.1043\,T^{1/2} + 0.3265\,P^{1/2} - 65.575$$

Inclusion of solid and gas residence time as variables did not produce any statistically significant correlation terms. Apparently, most of the oil is produced quickly, and longer contact times do not greatly influence the oil yield.

(d) UNIVERSITY OF UTAH

In the University of Utah process (Wiser, Anderson, Lytle), the coal is impregnated with 6 percent zinc chloride catalyst and hydropyrolyzed in a coiled-tube reactor at 493°C and 12.41 MPa (1800 psi). Residence time varies from 10 to 720 sec. From the test data for 24 coals, with carbon contents varying from 62 to 78 percent daf (from six coal fields of Utah), a multiple linear regression analysis gave the following correlation of conversion with coal properties:

% Conversion, daf basis (= liquid + gas yield) = −13.23 − 1.264 (% dry ash) − 1.437 (% daf C) + 31.52 (% daf H) + 29.04 (FSI).

It is worth noting that, in the equation, the term containing "free swelling index" is positive. The equation was not tested by comparing the predicted conversion reactivity with a set of data from entirely different coal feeds, but from experience with Utah coals, it seems reasonable to conclude that plasticity, the formation of liquid or semi-liquid phase in the coal particle could serve to wet the reactor wall. Such wetting determines the critical residence time in the coiled reactor and promotes the reaction.

PROCESS DESCRIPTIONS

In this section a number of processes under development will be surveyed very briefly, following the format in Tables 7 and 8. Each process (Howard-Smith, Werner, 1976, and Ralph M. Parsons Co., 1976) will be described as to the history of its development, specific features, test data, and development status.

Since many processes may be developing rapidly, rendering information quickly out-of-date, this review will emphasize test data, especially regarding feed coals, process conditions, product yields and product quality.

PYROLYSIS REACTORS

Three types of pyrolysis reactors are of commercial interest: (a) mechanically agitated (e.g. TOSCOAL process); (b) entrained-flow (e.g. Occidental process); and (c) fluidized-bed (e.g. COED, COALCON and C.S.I.R.O. processes).

Agitated reactors are mechanically complex; wear and erosion cause high maintenance costs and may create fine char particles which necessitate filters and electrostatic precipitators downstream.

Entrained-flow reactors, either upflow or downflow types, have short residence times. Throughput is high and reactor size relatively small. The Occidental reactor, a downflow type, showed reduced tendency to plug with agglomerating coals. Since its feed is

TABLE 7.
Pyrolysis Process Information Extract

Process	Coal Tested	Capacity	Status	Reactor-Type	Residence Time	Tar & Oil Yield Barrels/Ton Coal
OCCIDENTAL	Bituminous Subbituminous	3 TPD	PDU	Entrained-bed	1-3 sec	1.6
TOSCOAL	Bituminous Subbituminous Lignite	25 TPD	Pilot	Rotating Drum	? min	0.7-1.3
LURGI-RUHRGAS	Bituminous Brown Lignite	880 TPD	Commerical	Tubular Screw	20 sec. plus	1.1
COED	Bituminous Subbituminous	36 TPD	Pilot	Fluidized-beds	1.4 hrs	1.1
COALCON	Bituminous	16 TPD	Pilot	Free-fall dilute-phase	20-25 min	1.6
C.S.I.R.O.	Bituminous Sibbituminous	50 lb/hr	Bench Unit	Fluidized-bed	10-40 min	0.5 or less
SRT-CITIES SERVICE	Bituminous Subbituminous Lignite	2 lb/hr	Bench Unit	Entrained-bed	0.1-sec	0.6
SRT-ROCKETDYNE	Bituminous Lignite	0.25 TPD	Experimental	Entrained-bed dense-phase	0.05-0.3 sec	2-2.8
BNL	Lignite Subbituminous	0.5 lb/hour	Experimental	Entrained-bed down-flow	2-20 sec	1.2
SCHROEDER	Bituminous Lignite	1 lb/hr	Experimental	Fluidized-bed Catalytic	20-40 sec ?	3.0
UNIVERSITY OF UTAH	Bituminous Lignite	50 lb/hr	Experimental	Coiled tube turbulent flow	2-6 sec	2.4 or more
NCC-CARBONIZATION	Bituminous Subbituminous Lignite	220 TPD	Commercial	Moving Bed	? hour	0.7 or less

TABLE 8.
Pyrolysis Process Information Extract: Operating Conditions

Process	Temperature (a) °C	Pressure psi	H_2-partial pressure psi	Gas velocity ft/sec	Residence time second	H_2/Coal weight ratio	Particle size microns	Carbon Conversion daf %
OCCIDENTAL	590-870	65	-	15	3 (b)	-	60	45-60
TOSCOAL	425-540	15	-	-	300-600 (c)	-	1.27×10^6	25-35
LURGI-RUHRGAS	425-600	15	-	-	1-5 (b)		5×10^4	40-50
COED	150-870	17 - 27	-	2.6-6	180-960 (b)	-	3×10^5	40-50
COALCON	300-560	-	330	1	1500 (c)	0.04	140	50-60
SRT-CITIES SERVICE	530-940	500-2960	500-2960	0.5-77	0.7-25 (b)	0.08-5.1	45-400	30-55
SRT-ROCKETDYNE	700-1100	500-1500	470-1440	10-82	0.03-3.4 (b)	0.2-0.6	36-56	38-65
BNL	475-780	-	1000-3000	0.2-0.5	16-56 (b)	0.5-5.8	150	17-63
SCHROEDER	475-650	2000	-	-	20-30 (b)	1.4-2	300	60-90
UNIVERSITY OF UTAH	425-550	2000	-	-	1-6 (b)	1-2	250	56-70

(a) either the temperature of reactor wall, reactor bed or outlet gas-temperature
(b) gas-residence time
(c) solid residence time

fine (50-60 micron particles), it can be heated very rapidly.

Fluidized-bed reactors have been used successfully to process noncaking coals in Process Development Units (PDU) in the COED and COALCON programs. The commercial reactor used in the C.S.I.R.O. program has a 20-foot diameter and operated successfully. The U.S. Steel Clean Coke process utilizes a hydrocarbonization section that recycles a hot hydrogen-rich gas stream to provide the heat of the reaction and to remove sulfur as hydrogen sulfide.

PROBLEM AREAS FOR COAL PYROLYSIS PROCESSES

There are several problems specific to pyrolysis processes. Among these are:

(a) pressurized dry coal feed system; lock hoppers are the best available technology for pressurization, but are inefficient and frequently experience erosion;
(b) agglomeration and plugging: Rockwell, Westinghouse and Union Carbide have developed methods for handling caking coals in pyrolysis reactors, but experience in large scale operation is lacking;
(c) process heat for the reactor; in multistage pyrolysis processes (e.g. COED) heat is provided by combustion and/or gasification of char but in hydropyrolysis processes the problem has not yet been considered;
(d) recovery of reactor-effluent heat; the rapid quench of high temperature reactor effluents required in flash pyrolysis processes complicate heat recovery;

(e) down-stream cleanup minimizing the carry-over of unreacted solids with the liquid products demands efficient solid/gas separation; the cyclones and similar techniques have to be tried for this purpose.

REACTION PARAMETERS

The overall chemistry of coal pyrolysis processes depends on the rate of devolatilization and cracking of the volatile components of the coal and of carbon-gasification with reactive gases in the reactor. Temperature, pressure, particle sizes, gas-residence time, solid-residence time, heating rate and space velocities are all variables which control the extent of carbon-conversion and determine the product slate. Data from over 500 tests using lignite, subbituminous, and bituminous coals are available in literature.

For convenience, the operative conditions of individual processes are compiled in Table 8. Further details and the effects of the variables will be discussed in the narrative section that follows.

PROCESSES UNDER DEVELOPMENT

Occidental (Garrett) Flash Pyrolysis

Dried, pulverized (-200 mesh) coal is transferred pneumatically into an entrained-flow pyrolysis reactor where it is mixed with hot recycled char. The product vapors are separated from the solids and then condensed by scrubbing with a cooled recycle oil. The hot product char is separated from the product vapors by cyclones, transported to a char burner where it is heated to 650° to 870°C by the addition of a controlled quantity of air, then recycled. The reactor operates at 25 psi (170 kPa). Particle heat-up time is about 0.1 seconds.

A schematic diagram of the Garrett process is shown in Figure 6, and test data from a bench-scale reactor (1 lb/hr capacity) are given in Table 9.

TABLE 9.
Test Data from Occidental (Garrett) Process

Coal	West Kentucky		Wyoming
Coal Analysis, % daf:			
C	80.3		76.4
H	5.46		4.75
N	1.64		1.10
S	3.0		0.9
Fischer Assay, g/100 g Carbon:			
Tar	22.2		14.8
Gas	6.8		17.3
Operating Conditions:			
Temp., °C	593	593	870
Press., psi	65	65	65
Res. Time, sec	3	3	3
Space-velocity, ft/sec	15	15	15
Product Yield:			
Tar, g/100 g Carbon	47.6	22.2	17.4
Gas, g/100 g Carbon	8.9	16.1	36.3
Density of Tar, g/cc	1.1	1.1	1.1
Gas HHV, Btu/scf	700.0.	-	646.0

The test data demonstrated that the pyrolysis of coal under Garrett's processing conditions provides liquid yields 1.5 to 2 times greater than normal Fischer assay. Perhydrous coals yield more liquid than subbituminous coals. At reaction temperature above 600°C gas-yields increased at the expense of liquids, probably by extensive cracking of primary liquid vapors. Results from the pilot plant at LaVerne, California (4 ton/day, constructed in 1971) operating with a Wyoming subbituminous coal (Monarch-C, Big Horn Mine), almost duplicated the results from the bench-scale operation (Table 10).

Approximately 50 percent of the coal was converted to char in pilot plant operations. Recent experiments, however, using Kentucky No. 9 and Wyoming Monarch seam coals, indicate that initial PDU tar yields were low compared to projections from the BSR unit because of tar cracking on the excessively reactive surfaces of the recycle char (Sass, 1975).

TABLE 10.
Comparative Data of Occidental (Garrett) Process for PDU and BSR Units

Coal analysis: Moist 11.0; Ash 5.7
Analysis, % daf: C 73.3, H 5.3, N 1.2
S 0.7, O 19.4.

Reaction Conditions & Properties of Liquid Products	PDU	BSR
1. Reactor Temperature °F	1050	1000
2. Particle Residence Time, sec	2.5	3.0
3. Liquid Products, API Gravity	-8.6	-8.1
4. Liquid Viscosity, 250°F, C_p	115	135
5. Liquid Pentane-solubility, Wt%	54.9	56.4
6. Liquid Asphaltene content, Wt%	28.0	27.4
7. Liquid Py-sol but Toluene-insoluble	14.8	16.1
8. Liquid Pyridine-insoluble, Wt%	2.2	0.1
9. Liquid Distillation characteristics:		
- 50% fraction distilled at °F	730	800
- I.B.P. (ASTM-D-1160), °F	430	500

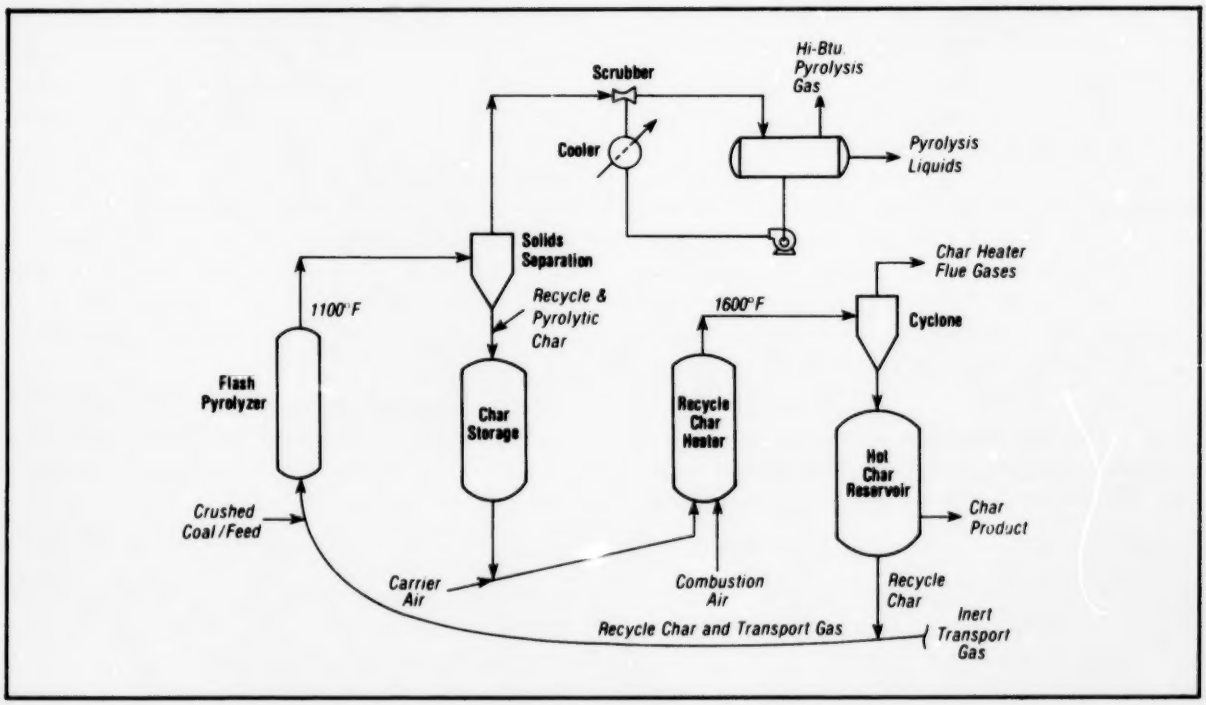

FIGURE 6. Occidental (Garrett) Coal Flash Process: flow diagram.

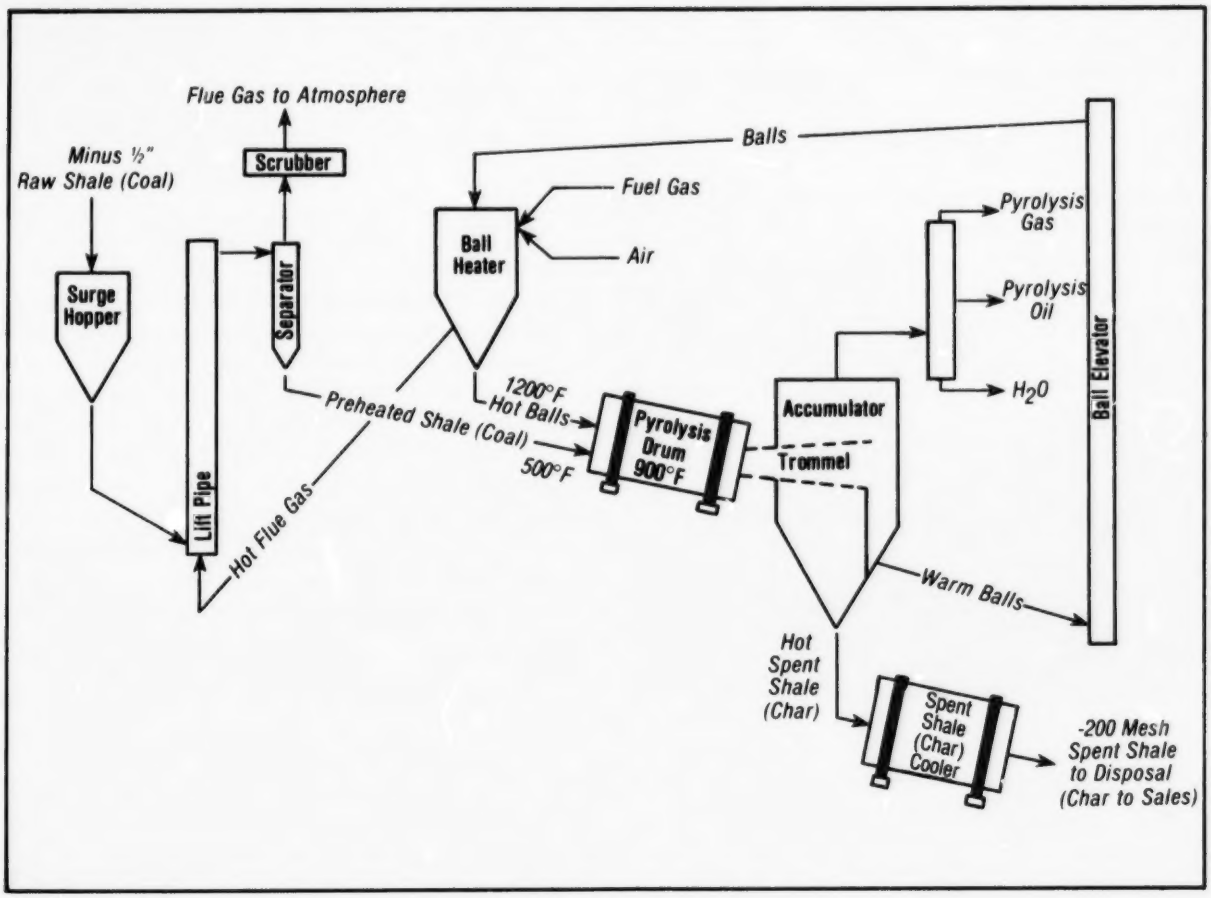

FIGURE 7. TOSCOAL Pyrolysis Process: flow diagram.

TABLE 11.
Test Data in TOSCOAL Process
(Based on Wyodak Coal, daf C% 71.5, H% 4.3, N% 1.1, S% 0.4)

Product (per 100 g Carbon)	Fischer assay		Retort	
Temp: °C	510	425	485	520
Tar-liquid, g	19.1	12.2	15.4	20.1
Gas, g	16.5	12.9	15.4	13.6
Total, g	35.6	25.1	30.8	33.7
Gas yield, dry feed				
scf/ton	2780	1786	2539	2321
Btu/scf		494	663	580

TOSCOAL Process

The Oil Shale Corporation is adapting the TOSCO II oil-shale retorting system to low temperature pyrolysis of coal. The objective is to upgrade the heating value of subbituminous coals to reduce the transportation costs, and to recover hydrocarbon liquids as by-products. A 25 ton/day pilot plant has been located at the Rocky Flat Research Center near Golden, Colorado since 1975.

In this process, crushed coal is dried and preheated by hot flue gas before being transported to the carbonization drum where it is mixed with hot ceramic balls. The pyrolysis temperature is between 430°C and 520°C, at 0 to 34 kPa (0 to 5 psi) pressure. After a residence time of approximately 5 to 10 min in the drum, the products are removed and passed through a trommel screen. The cooled ceramic balls pass over the screen and are returned to a ball heater fueled by a portion of the product gas. The flue gas from the ball heater is used to precondition the coal. The product stream is separated into solid and vapors. The latter are condensed and fractionated into liquids and gases. Figure 7 is a schematic diagram of the process.

The advantage of this process is that indirect heating, using a ceramic ball as a heat transfer medium, eliminates the dilution of product gas with nitrogen and combustion products. The optimized product yield parallel the Fischer assay results (Table 11).

TOSCOAL Oil has high viscosity and requires refining by hydrogenation or conventional tar-refining processing (Carlson, 1975).

Lurgi-Ruhrgas Process

The Lurgi-Ruhrgas process is conceptually similar to the Garrett process. The pyrolysis char is circulated as a heat carrier to devolatilize the coal in a mechanical mixer. A schematic diagram of the process is shown in Figure 8. The plant is designed to operate in close conjunction with a thermal power station fueled by the product char (Rammler, 1970).

In the original design, 5 to 6 mm particles of dried coal are fed with hot char to a mechanical mixer which ensures rapid heating of coal for 1 to 2 sec. Liquid yields are optimized by a reaction temperature of 600°C followed by a rapid quench. The pressure of the system is maintained between 0 and 34 kPa (5 psi).

In a modified, two-stage process, which has not yet been tested on a pilot plant scale, gas yields are improved by post-devolatilizing the coal in the surge-hopper at 900°C by adding hot char downstream from the mechanical mixer.

A small commercial plant with capacity of 800 ton/day has been in operation at Lukavac, Yugoslavia since 1963. A large scale pilot plant to processs 265 ton/day of caking long-flame subbituminous coal from Furst Leopold Colliery is in operation at Dorsten, West Germany.

Optimum liquid yields obtained from coal of 45.5 percent volatile matter content are estimated at 1.4 to 1.6 bbl/ton of daf coal. At the Dorsten pilot plant, liquid yields of 180 percent of the Fischer assay have been achieved. Typical gas yields are 1530 to 3320 scf/ton (60 to 130 m^3/ton) with heating value on an air-free basis ranging between 625 and 750 Btu/scf. It is estimated that in the two-stage process, net calorie output in gas and liquid products would increase by a factor of 1.3.

The liquid product has a density of -4° API (1.109 kg/m^3). The char from the mixer contains approximately 8 percent volatile matters.

COED Process

COED is a slow pyrolysis process in a moving bed. Its novelty lies in its sweeping of volatile products from the reaction at several different stages, using hot flue gas which also functions as a heat carrier. Figure 9 is a flow-diagram of the 36 ton/day pilot plant.

Dried coal, sized to minus 3.2 mm, is cascaded through a series of low-pressure (41 to 69 kPa) fluidized-bed reactors maintained at successively higher temperatures. A typical temperature series is 320°, 450°, 540°, and 870°C in successive reactors. The temperature of each bed is selected to be immediately below the maximum temperature to which its feedstuff, coal or intermediate char, can be heated without agglomerating and defluidizing the bed. The aggregate feedstock residence time is several hours.

Hot gas, generated by burning a part of the char with oxygen in the fourth stage, is used for fluidization and devolatilization by countercurrent flow in the third and second stages.

Exit gases are quenched, either in circulating liquor (first stage) or directly in water (second stage) to condense the oil. The oil is then separated from the water and passed through a rotary-drum precoat filter to remove char carryover. The separated gas is purified and steam-reformed to produce hydrogen which is then used for hydrotreating the liquid in a fixed bed catalytic reactor with a nickel molybdate catalyst.

The original COED process was designed to utilize char which had been devolatilized for thermal generation of electric energy. A modified process, known as COGAS process, has been developed to generate a synthetic medium-Btu gas, as well as oils. It uses the fourth reactor as a

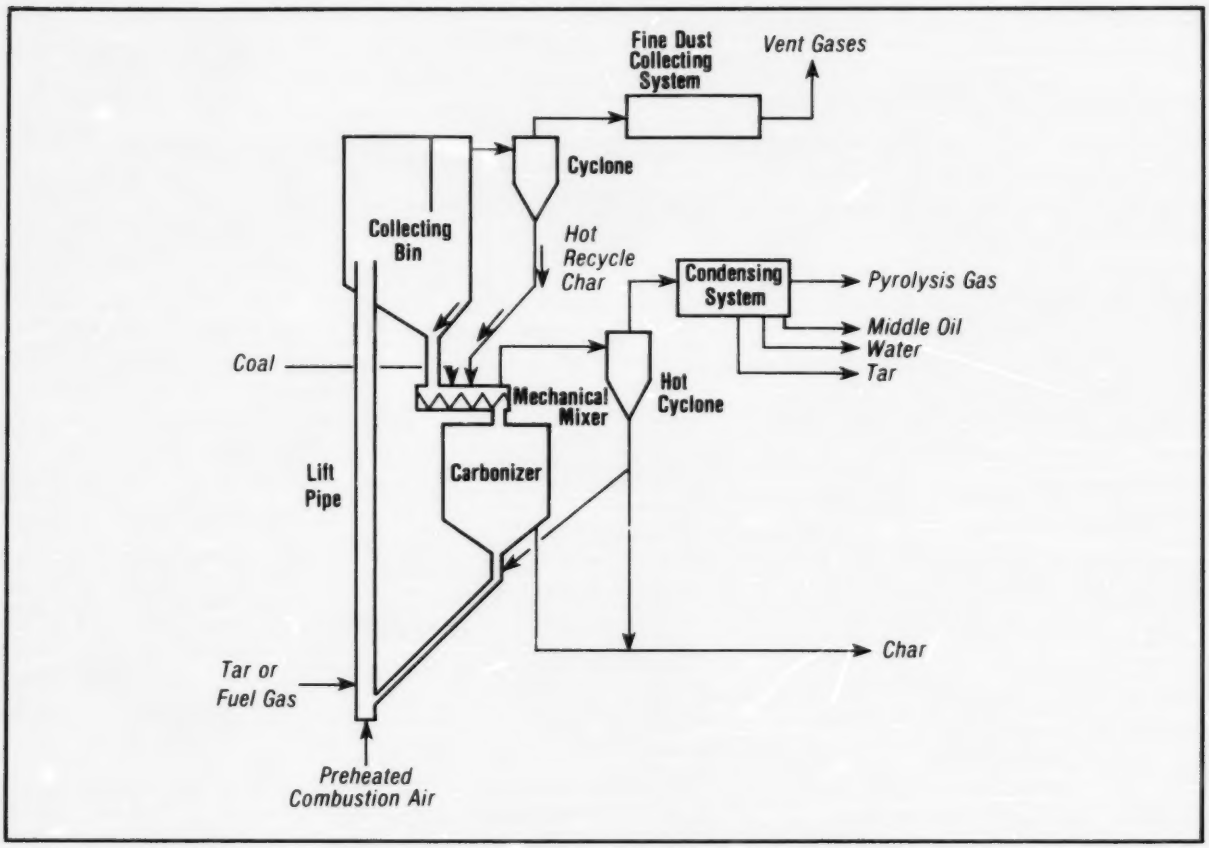

FIGURE 8. Lurgi-Ruhrgas Process: flow diagram.

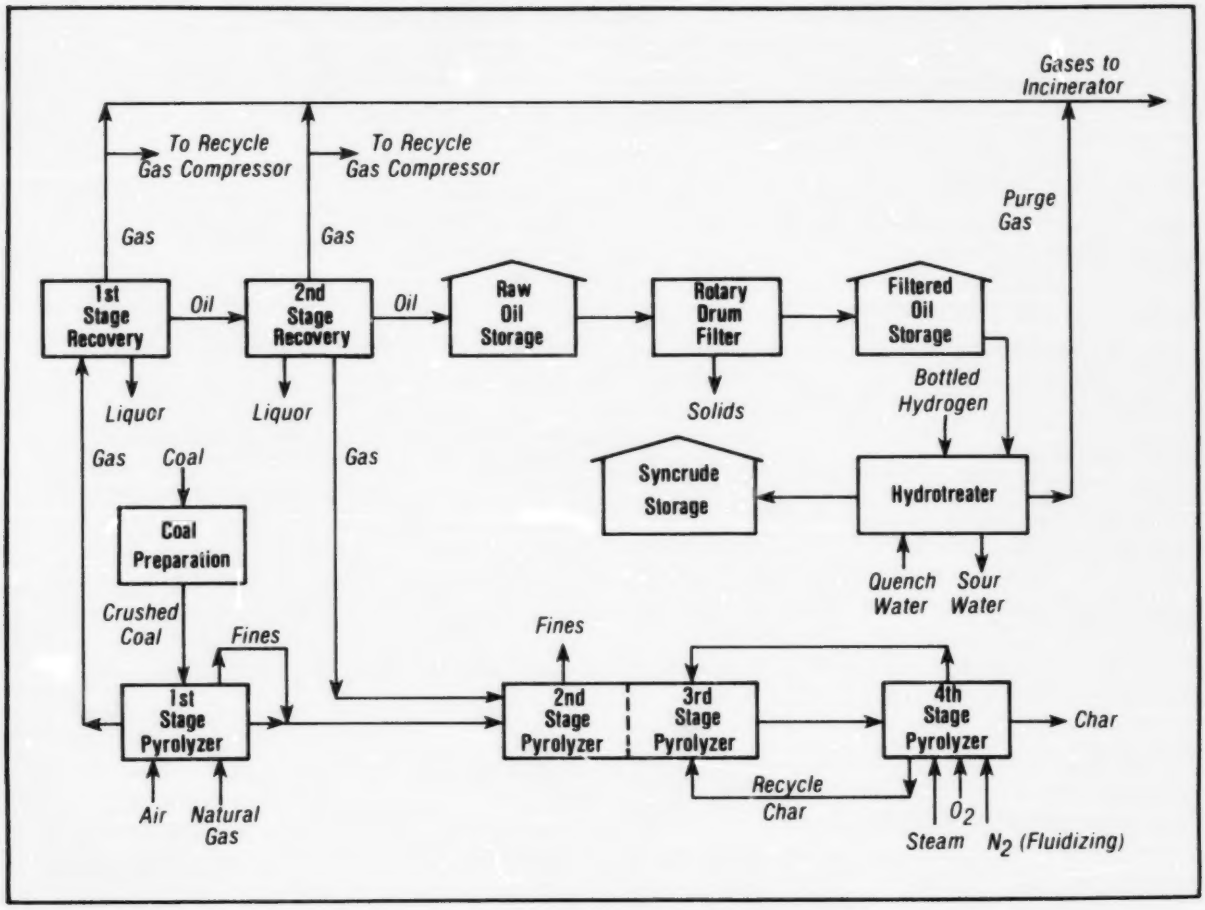

FIGURE 9. A 36 ton/day COED Pilot Plant: flow diagram.

gasifier, partially reacting the char with steam at 1600°F to form a mixture of hydrogen and carbon monoxide. Exiting, unreacted char is burned to generate a solid heat carrier which is recycled to the gasifier. The advantage of both COED and COGAS processes lies in their ability to handle agglomerating coals continuously without any difficulty (Merrill, 1975).

A 36 ton/day COGAS pilot plant was constructed by the FMC Corporation at Princeton, New Jersey. It operated from August 1970 to April 1975 to process a variety of American coals. Typical product distributions from pyrolysis of subbituminous and bituminous coals in this plant are summarized in Table 12 (from Berkowitz, 1979).

Product oil from the COED process typically has a density of approximately -4° API (1.109 kg/m^3). The hydrogen required to upgrade this liquid to sweet synthetic crude oil (22.5° API) is estimated at 3000 scf/bbl. COED naphthas are typically 73 percent naphthenes, 7 percent paraffins and 20 percent aromatics. Depending on the coal type, the heating value of the product gas varies from 550 to 650 Btu/scf. Overall thermal efficiencies for the COED process are reported to lie in the 89 to 90 percent range.

TABLE 12.
Product yields from COGAS pilot plant

Yield wt % dry coal	hvb coal Illinois	hvb coal Utah	Subbituminous Coal Wyoming
Char	60.7	59.0	50.0
Oils	18.7	21.9	11.2
Aqueous liquor	5.8		11.6
Gas*	14.6	21.5	27.2

*Excluding gas from downstream char gasification

COALCON Process

The Coalcon Company, a joint venture of Union Carbide and Chemical Construction Corporation, was funded by the U.S. Office of Coal Research in January 1975 to design, construct and operate a 2370 ton/day coal hydrocarbonization plant. The Dravo Corporation conducted an economic evaluation of this operation in 1976.

The COALCON process (Coles, 1976) is an advanced version of experiments carried out at Pittsburgh Energy Research Center to study hydrocarbonization of high sulfur coals in a free-fall, dilute-phase reactor. Using a series of bench-scale units (1 lb/hr and 10 lb/hr) and a pilot plant (16.8 ton/hr), Union Carbide obtained fundamental data for the process and, in the pilot plant, demonstrated long-term successful operation.

In the COALCON process, 0.075 to 0.42 mm sized coal is heated in the presence of make-up and recycled hydrogen in a fluidized bed. Solids residence time in the bed varies between 20 and 25 min, the operating temperature is 560°C, and pressure less than 1000 psi (6.90 MPa). The char is gasified for hydrogen and SNG production.

The following test data were obtained by processing Pittsburgh No. 8 coal (%C 81.0, %H 5.6, %N 1.5, %S 2.9, daf) using space velocity of 60 to 70 lb/hr and H_2-partial pressure of 330 psig:

Product Yield	%Dry, ash-free Coal basis	gram/100 g Coal-carbon
Char	43.0	51.1
Liquids	31.9	39.4
Gas	24.2	30.0

The hydrogen consumption was 3.9 lb/100 lb coal (daf).

It is estimated that typical yields in the COALCON process from one ton of bituminous coal would be 2.1 bbl of liquid product and 8673 scf of SNG with a heating value of 1000 Btu/scf. Thermal efficiency was estimated to be 62.4 percent by the Dravo Corporation.

Of the COALCON liquid products 65 percent are aliphatic, 21 percent naphthanic, 7 percent ketonic and 7 percent aromatic. On distillation, the liquids yield 10 percent light oils (pentanes, hexanes and BTX), 45 percent light oils of complex composition, 15 percent middle oils, 10 percent pasting oils and 10 percent pitch.

C.S.I.R.O. Process
(Commonwealth Scientific and Industrial Research Organization, Australia.)

The C.S.I.R.O. continuous fluid bed process (Smith, 1980) is designed to use weakly agglomerating, high-volatile Australian coals as feedstock. Operating at high temperatures, it converts the coal

mostly to a medium-Btu gas, but with lowered temperatures it increases the yield of tars and chars.

An experimental unit with nominal capacity of 50 lb/hr was built to process Wallarah seam coal (daf C% 84.3, H% 4.9). The unit consists of a coal-feed hopper, a carbonizer, a char receiver, a by-products recovery train, a gas holder and a small compressor for blowing fluidizing gas into the carbonizer.

The crushed coal is conveyed by a variable-speed screw-feeder to the carbonizer where a controlled stream of preheated gas maintains a fluidized bed. As carbonization of the incoming coal proceeds, the bed overflows and char is discharged through an off-take into a bin. To prevent agglomeration, part of the char is blended continuously back with the incoming coal. When air is used as fluidizing gas, heat for the process is supplied mainly by combustion and the main product is gas. When hydrogen-rich, recycled gas is used for fluidization and electrical heaters are immersed in the bed to supply the reaction heat, significant amounts of tars and chars are produced. Gas and volatile products are separated in the by-product train.

Results from the experimental unit show that hydrogenation of the coal takes place in two well-defined stages. When the hydrogen partial pressure is increased at a given temperature, the yield of hydrogenation products, such as methane and water, increases and the yield of pyrolysis products, such as CO, CO_2, H_2, tar, and carbon, decreases. By adjusting the process conditions, the combustion reactions accompanying hydrocarbonization can be manipulated to produce optimum yields of either gas or tar as needed.

In the experimental unit, tar yield from low temperature carbonization (460°C) was 9.3 percent, twice the yield in the Fischer assay (static bed at 500°C) which was 4.3 percent. Some representative experimental data are presented in Table 13.

Short Residence Time (SRT) Coal Hydropyrolysis Process
(Cities Service SRT Process)

The Cities Service Process (Pelofsky, 1976) is now emerging from the conceptual stage. To date, experiments have been conducted with a bench-scale (2 lb/hr) unit featuring a free-fall dilute phase, externally heated reactor suitable for North Dakota lignite. The equipment configuration for this unit is shown in Figure 10. The plant flow sheet is shown in Figure 11.

In the Cities Service bench-unit, pulverized dry coal (50 to 450 micron) is fed from pressurized coal hoppers by a star-wheel feeder into the reactor. A proprietary nozzle arrangement mixes the coal with hot hydrogen and ensures that the coal is heated very rapidly at a rate of 50 000 to 150 000°F/sec. The reactants then are quenched by cryogenically cooled hydrogen in the cooler. The quenched products are separated in a solid receiver at the end of the reactor tube into a char and ash split and a gaseous product split that, in turn, is cooled to recover several liquid fractions.

In one conceptual plan it is proposed that hydrogen make-up be provided by steam-reforming part of the product gas (methane). Char would be gasified with air to provide fuel gas to fire the reformer and to generate electricity. An alternative concept would use coal and char gasification with steam and oxygen for hydrogen make-up.

The original bench unit, located in Cities Service research and development laboratories in Cranbury, New Jersey, began operating in the summer of 1975. Lignite and a western Kentucky bituminous coal have been tested with most runs lasting 4 to 5 hours. The unique feature claimed for the process is a noncatalytic hydropyrolysis reaction that yields 12 to 16 percent (based on daf coal) light aromatic oil (essentially benzenes) and 34 to 68 percent high Btu gas (largely methane). Representative test data are shown in Table 14.

TABLE 13.
Results from C.S.I.R.O. Process, Australian Coal

At low temperatures						
Feed-rate, lb/hr	33.5	35.2	37.5	35.5	51.4	102.4
Residence time, min	33.5	32.2	33.4	36.9	26.4	13.8
Reaction Temp., ^{o}C	500	550	460	460	500	500
Fluidizing Gas	air	air	air	H*	H*	H*
Yields, w/w % coal						
dry tar & pitch	6.7	7.2	4.9	9.5	8.7	3.1
Composition w/w %						
Tar acids	31.0	33.6	26.4	39.6	38.1	39.2
Tar bases	2.0	3.2	2.4	2.3	2.6	2.9
Neutral oils	67.0	63.2	71.2	58.1	59.3	57.9

At high temperatures and varying H_2-partial pressure			
Reaction Temp., ^{o}C	736	754	853
Pressure, psi	308	603	603
H_2-partial pressure, psi	200	400	493
Feed rate, coal, daf, lb/hr	8.88	36.01	9.97
Products, fraction carbon			
Gas, CH_4 + other	0.247	0.242	0.416
$CO + CO_2$	0.131	0.094	0.100
Tar	0.059	0.058	0.010
Char	0.570	0.606	0.473

H* = recycle gas with H_2 varying from 40 to 80%.

TABLE 14.
Test Data from SRT-hydropyrolysis Process (Cities Service)

Coal:	North Dakota Lignite: %C 61.3, %H 4.1, %N 1.2, %S 1.4
Hydrogen/Coal ratio:	0.18 to 2.0 lb/lb
Reactor Temperature:	1150 - 1575^{o}F
Reactor Pressure:	500 - 3000 psi
Quench Temperature:	450 - 1000^{o}F
Residence Time (Particle)	100 - 3000 msec
Yield (daf coal)	
Gas, scf/ton	19 310
Liquids, bbl/ton	0.63 (16.3 g per 100 g coal-carbon)

Notes:

a. With increasing particle residence time beyond 50 msec, BTX is cracked to coke and hydrogen.

b. Carbon selectivity to liquid is maximum at 43 percent conversion level; higher conversion level produces mostly methane.

c. Carbon conversion increases with coal heat-up rate.

d. Carbon conversion increases with reaction temperature (1200 to 1550^{o}F) to an asymptote at about 46 percent.

e. Hydrogen consumption at this level is 6.8 wt% of daf coal or 25 595 scf/ton of daf coal or 40 630 scf/bbl oil.

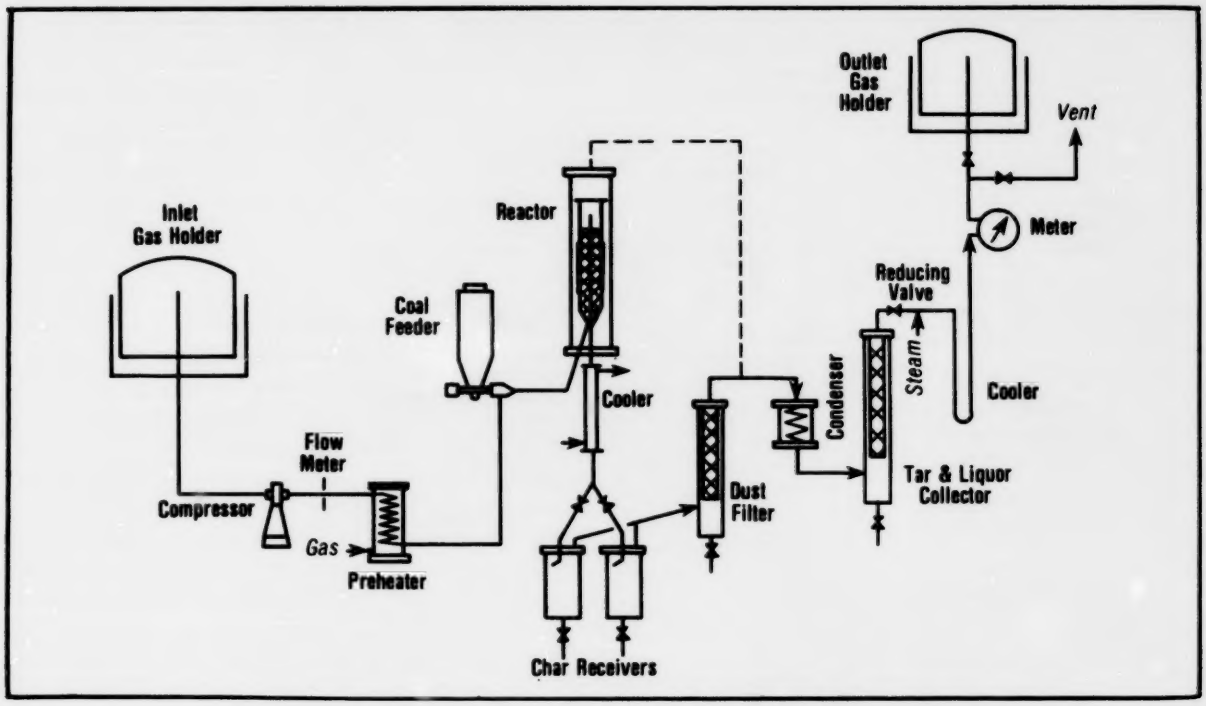

FIGURE 10. SRT-Cities Service Process: Equipment Configuration.

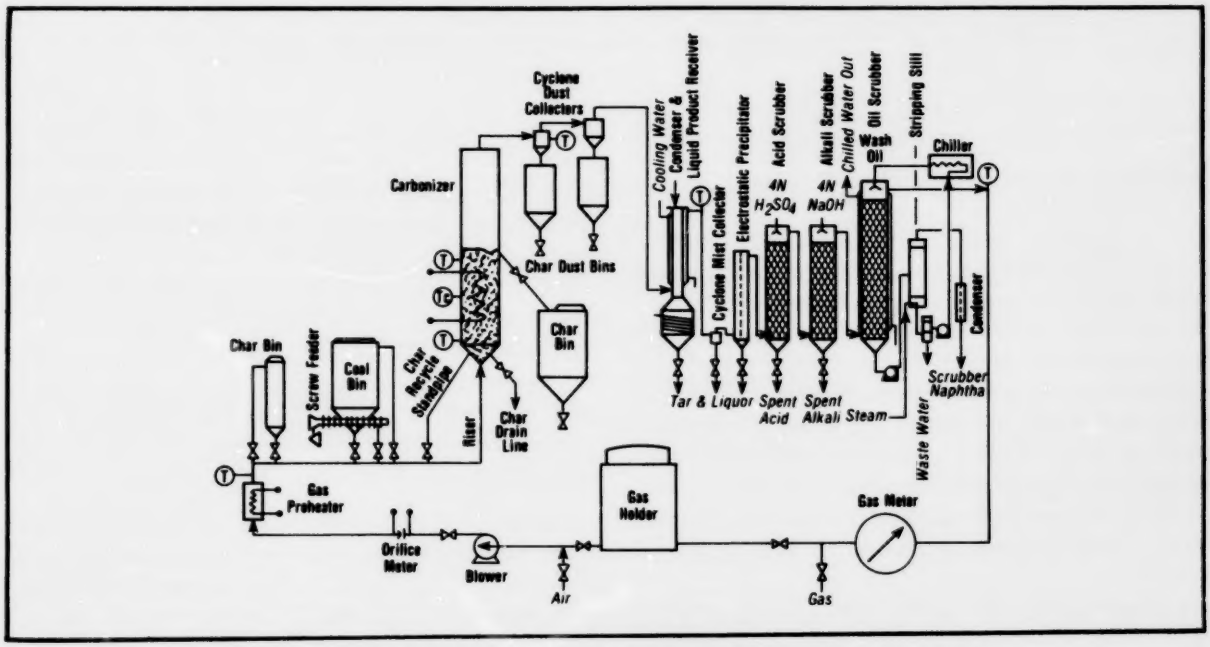

FIGURE 11. SRT-Cities Service Process: Equipment Plant Flowsheet.

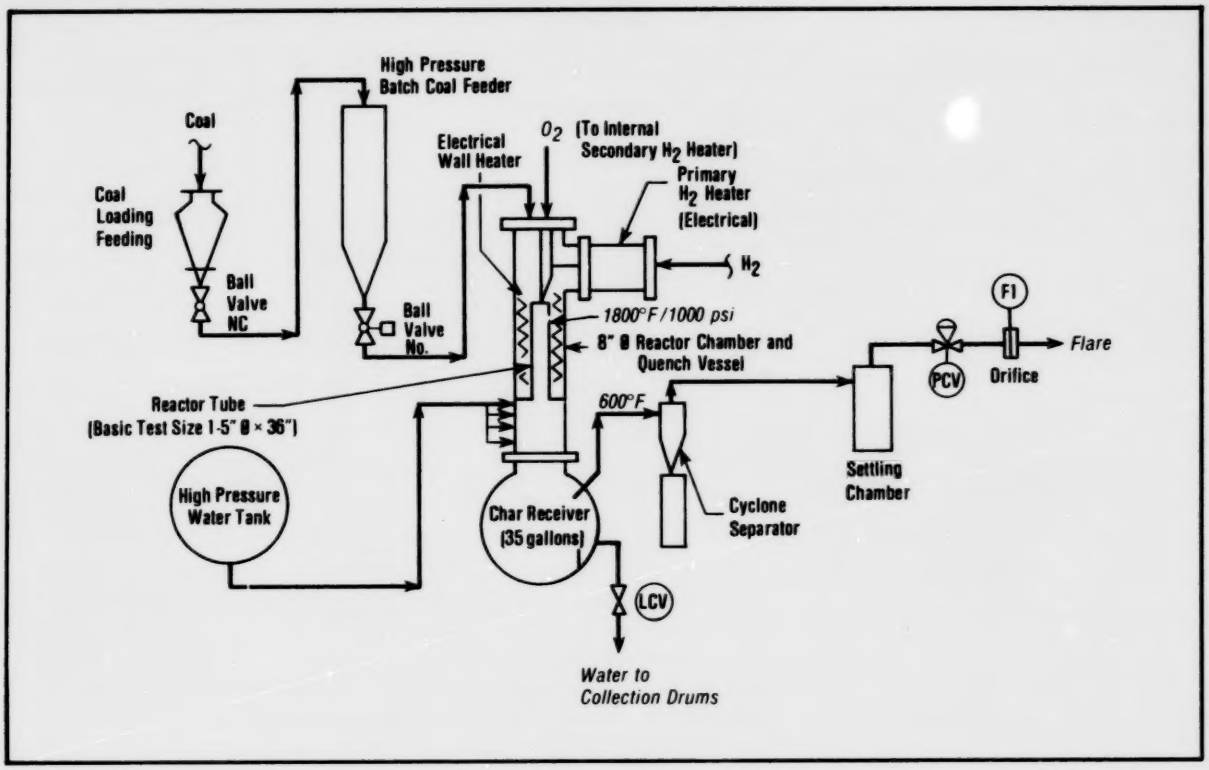

FIGURE 12. SRT-Rocketdyne Process, 0.25 ton/hr reactor flow diagram.

Rocketdyne Flash-Hydropyrolysis Process

The Rocketdyne process (Durai-Swamy, 1979), featuring rapid hydropyrolysis of coal in a dense phase, has been jointly sponsored since 1975 by the Rockwell International Corporation, Canoga Park, California and the U.S. Department of Energy. It is still at a very early stage of development. Investigations were conducted in a 0.25 ton-per-hour reactor with a hydrogen preheater and an oxygen-hydrogen preburner that supplied heat to the process. Figure 12 shows the reactor system; Figure 13 shows detail of the reactor vessel itself.

Dry, pulverized coal (less than 150 micron), from a pressurized lock hopper, and hot hydrogen (1093°C) are fed downward to the reactor injector. Two types of injector nozzle have been tested, both of which ensure rapid mixing of materials: (1) a concentric tube type wherein the coal dust and hot hydrogen flow coaxially; (2) a 4-on-1 type wherein four hot hydrogen jet streams impinge on a central coal dust stream. The coal/hydrogen mix reacts for 30 to 100 msec in the downflow reactor before being quenched by water spray and heat exchange.

A highly volatile bituminous western Kentucky coal (%C 78.1, %H 5.7, %N 1, %S 4.4 and %VM 42.0) was tested in this reactor under the following operating conditions:

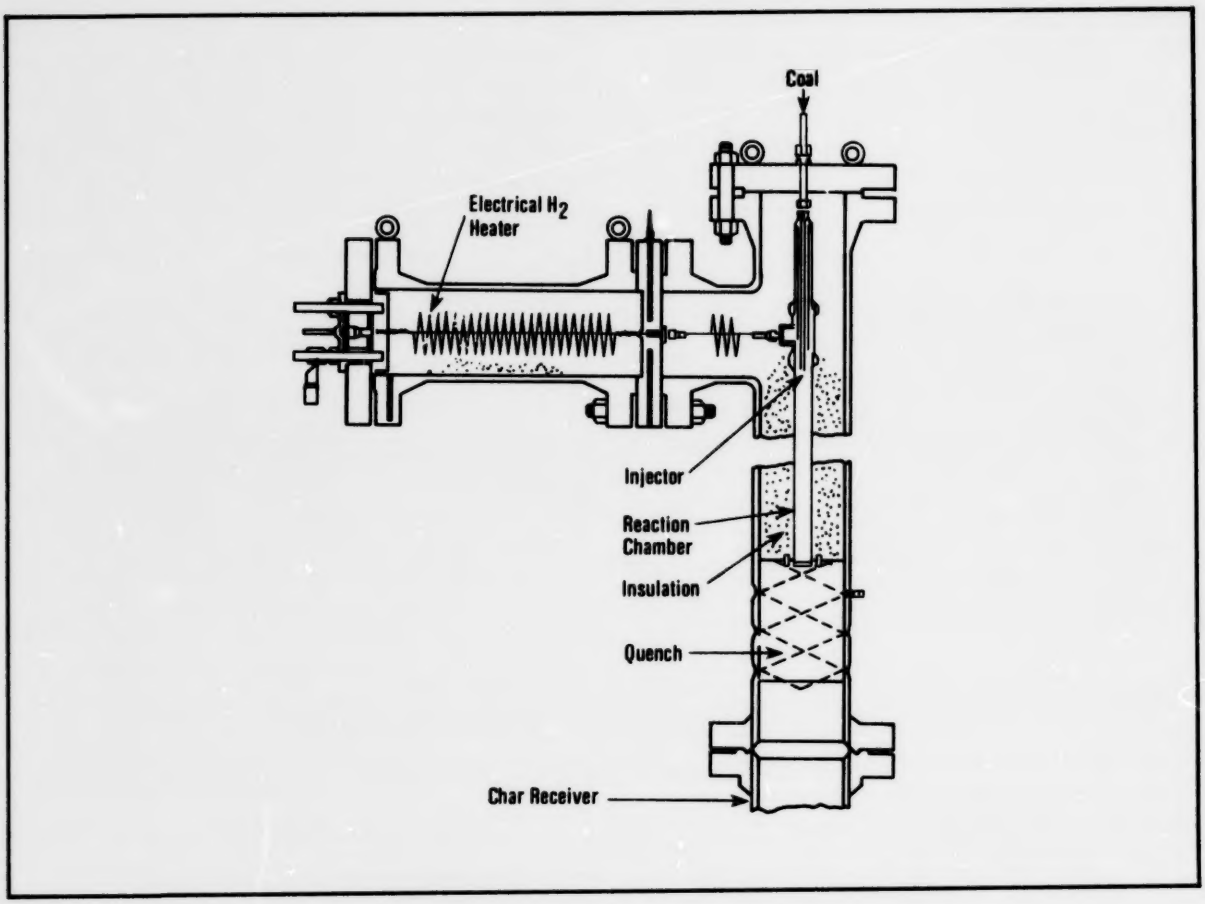

FIGURE 13. Rocketdyne 0.25 ton/hr reactor assembly.

Pressure	1000 psig
Temperature	530 to 1093°C
Coal/Hydrogen Ratio	38 to 114 scf H_2/lb coal
Residence time	50 - 300 msec
Particle velocity	10 - 30 ft/sec
Space velocity	23 000 - 3800 lb/hr/ft^3

An overall carbon conversion of 56 to 60 percent was achieved with the following distribution of products:

Gas 11.9% (C_1 to C_2 being 5.6%)

Oil 42.5% (40% boils below 530°C) (2.86 bbl/ton daf coal)

Char 45.6%.

Overall carbon conversion increased with increased temperature, as well as with increasing residence time. Liquid yields, however, reached a maximum of about 40 percent at a temperature of 1000°C and reduced to zero at residence time greater than 650 msec.

A 10 ton/hr facility is currently in the planning stage.

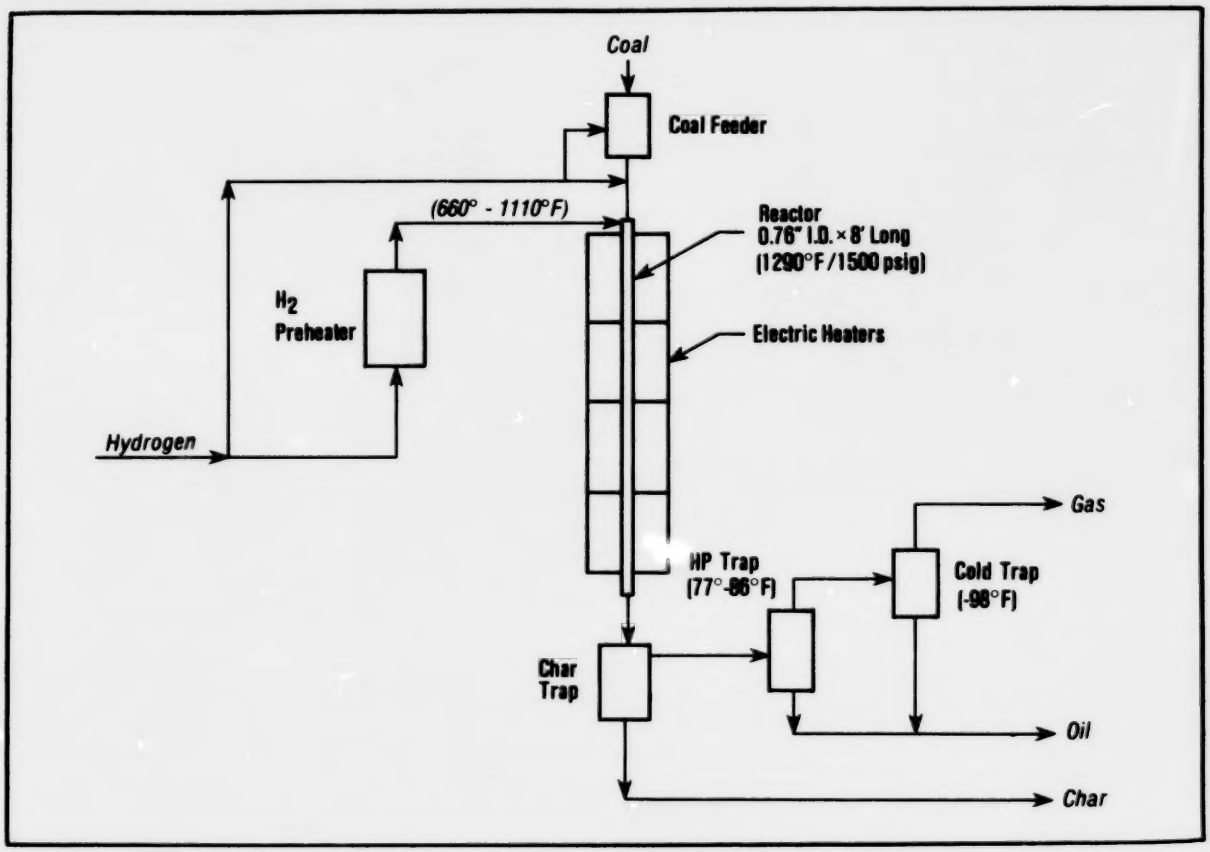

FIGURE 14. BNL Rapid Hydrogenation Process 0.5 lb/hr bench-scale unit flow diagram.

BNL (Brookhaven National Laboratory) Flash Pyrolysis Process

In the early 1960s, the U.S. Bureau of Mines studied rapid gas phase hydrogenation of coal at high temperatures and high pressures yielding aromatic hydrocarbons and light oils. Schroeder and others subsequently elaborated on this process concept. Beginning in 1975, Brookhaven National Laboratory, Upton, New York, has operated a 0.5 lb/hr bench-scale unit with a 1 in diameter x 8 ft long dilute phase reactor to evaluate this same process for its process chemistry and potential for scale-up (Steinberg ét al., 1978). Figure 14 shows this unit schematically.

Dry, pulverized coal (less than 150 micron) from a pressurized lock hopper and hot recycled hydrogen (980^{o}C) are mixed and fed to the entrained downflow tubular reactor. The products are quenched in a cooled receiver at the bottom of the reactor tube where solids are trapped, while gaseous products pass through at elevated temperatures and pressures. Gases are then cooled rapidly to recover oils that flow to an extractive distillation unit for benzene extraction.

Hydrogen for the pyrolysis is produced partly from char and partly from hydrocarbon vapors that have passed over. The char is separated in multi-stage cyclones and routed to a gasifier for hydrogen

production. Hydrocarbon vapors, after being cleaned in a quench tower, are directed to a gas separation unit for cryogenic separation of hydrogen from methane and ethane. To raise the coal to reaction temperature the hydrogen feed is preheated to 980^{0}C in a furnace fueled by CO recovered from the hydrocarbon vapors. The coal is brought to about 245^{0}C by the hot hydrogen then reaches a final temperature of 690 to 700^{0}C.

Test data with two coal samples are given in Table 15.

TABLE 15.
Test Data from BNL Flash Hydropyrolysis Process

i.	Process conditions:		
	Pressure	500 to 4000 psi	
	Temperature	700 to 815^{o}C	
	Residence time	2 to 18 sec	
	Hydrogen/coal	100 to 130 scf/lb coal	
	Space velocity	13 to 10 lb coal/hr/ft^{3}	
ii.	Coal	Lignite (N. Dakota)	Sub-bit (New Mexico)
	% C	68.9	77.0
	% H	4.7	5.8
	% N	1.1	1.7
	% S	1.3	0.7
iii.	Conversion % C		
	C_1-C_5 hydrocarbon and	47.00	37.00
	C_6 oil	19.1	12.9

Notes:

a. Conversion yield increases with increase in pressure.
b. Increase in residence time over 16 to 38 sec reduces the overall conversion yield, lowering the liquid yield but increasing the gas yield.
c. Increase in the space-velocity of the feed adversely affects the liquid yield.
d. Plugging of the reactor is a common problem with caking coal.
e. Short residence time provides higher BTX content of the product liquids. Maximum BTX content is achieved at 15 000 to 20 000 psi pressure and 700 to 800^{o}C temperature, with a 3 to 9 sec residence time.
f. Lignite is not reactive at temperatures below 630^{o}C. [In the static bed, lignite starts to decompose at 325^{o}C. Does it mean that in the BNL process, the particle temperature does not exceed 325^{o}C?]

A conceptual plant design for 25 000 ton/day of coal to produce 40 000 bbl/day of benzenes consists of the following modules:

1. coal preparation unit;
2. quasi-entrained flow tubular hydropyrolysis reactor;
3. liquid and gaseous products separation units;
4. char separation unit;
5. hydrogen recycle unit;
6. char-gasification unit;
7. end-products modification units.

In this plant, the hydrogen feed rate is determined by the requirements for heating lignite. By a heat balance it has been determined that 13.7 lb of hydrogen are required per 100 lb of lignite, of which 6 lb are chemically consumed. To produce the desired products, about 7.7 lb of recycle hydrogen per 100 lb of lignite must be introduced in the reactor feed.

Schroeder's Catalytic Hydropyrolysis Process

Early in 1960, Schroeder demonstrated in the laboratory that a non-caking bituminous coal, after being impregnated with ammonium molybdate, could be hydrocracked in hydrogen pressure of 100 atmospheres or more at 450 to 550^{0}C to yield more than 3 bbl of liquid products per ton of coal. Subsequently El Paso Natural Gas Company and Spencer Chemical Company sponsored a 1 lb/hr bench-scale reactor for further development work, using non-caking coals from Colorado, Missouri, Kansas and New Mexico, and three U.S. patents were issued (Schroeder, 1964; 1975).

The equipment, in Figure 15, centers around a tubular reactor to which dried catalyst-impregnated coal is fed from a pressurized feeder along with hydrogen, from a reformer, hot enough to effect the desired temperature. Products from the reactor are cooled and separated; the tar fraction is further hydrogenated to produce distillable oils and gases, which are combined with the oils and gases produced directly, passed through a cyclone separator and cooled. The separated oils are further refined; the gases, after purging of nitrogen/sulfur components and other impurities, are reformed with oxygen and steam to make hydrogen. The CO concentration in the recycle gas stream may be reduced by a shift conversion prior to purification. Representative test data are given in Table 16.

TABLE 16.
Test Data from Schroeder's Hydropyrolysis Process

pressure	136 atm, Temperature 500°C
hydrogen	254 scf/lb coal
gas residence time	29 sec
coal weight hourly space velocity	18.5 lb/hr/ft^3
coal mass velocity	145 lb/hr/ft^2
coal analysis	(New Mexico daf basis): C 84.5% H 5.6%, N 2.1%, S 2.0%
product yields	(wt % of carbon feed, excluding hydrogen manufacture and utilities):
hydrocarbon gas	37.3%
light oil	29.0% (alkyl-cyclohexanes, BTX)
heavy oil & tar	26.0%
char	7.6%
net carbon conversion	92.4% (7.6% used for hydrogen production and utilities)
thermal efficiency:	
production only	75%
overall	71% (including net utilities)
steam used/generated	1012 lb/hr
power	116 kw/hr
cooling water	262 gal
fuel (oil product for steam and power)	0.87 MM/Btu

Notes:

a. Preferred temperature to maximize liquid yield is 425 to 530°C and gas yield, 450 to 700°C. Above 700°C hydrocarbon products are essentially gaseous with only small yields of mostly aromatic liquids.
b. The conversion maxima correspond to a gas residence time of 15 to 20 sec depending on the pressure; at higher pressures, residence time is shorter for maximum liquid production.
c. Total conversion does not depend on particle size but liquid/gas ratio in the product does; larger particle size tends to produce less liquids.
d. Between 0.5 to 1.0 percent (1 lb/ton daf Coal) of the catalyst effectively increased the liquid yield between 425 and 530°C. Higher concentrations of catalyst or temperature above 530°C tended to lower the liquid/gas ratio.
e. New Mexico coal gave data typical of all the coals tested.

Conceptual pilot plant designs are available from Spencer Chemical Company, El Paso Natural Gas Company and Technip Inc.

The University of Utah Coal Hydrogenation Process

Beginning in 1972, the U.S. Office of Coal Research and the State of Utah jointly sponsored an extensive study on the catalytic hydropyrolysis of coal. Liquefaction and gasification of western coals were the major objectives. The original unit has a semi-continuous, free-fall, down-flow hydrogenation reactor with a disperse phase and short residence time in a hydrogen atmosphere. Over the period 1972-1979, the reactor configuration was progressively changed, finally evolving into the present 50 lb/hr bench-scale unit with a coiled tube, turbulent flow reactor capable of fast heat transfer from gas to solid particles (Wiser, 1975; Lytle, 1979).

The process equipment, shown in Figure 16, consists of (1) a pressurized dual coal hopper, permitting continuous operation at 2000 psi, connected with a rotary wheel feeder to feed

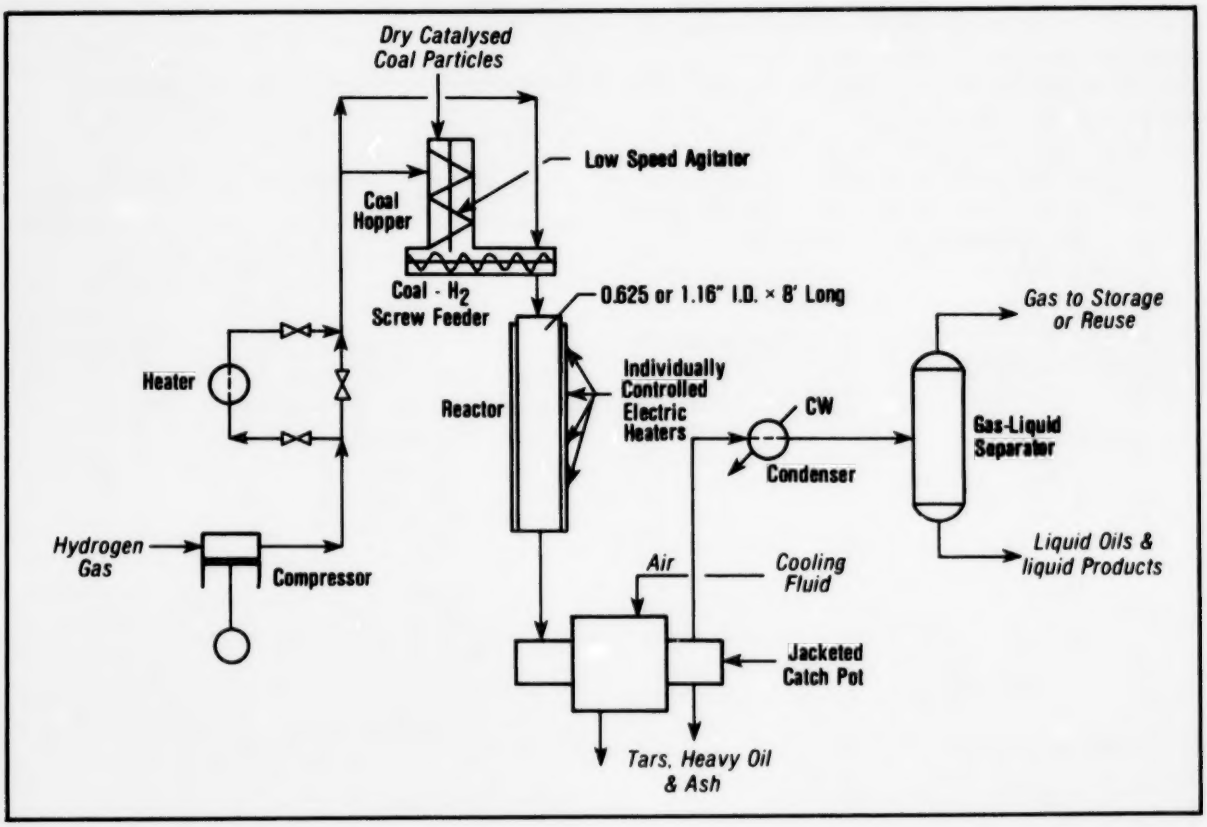

FIGURE 15. Schroeder's Catalytic Hydrogenation Process, PDU Flow Diagram.

3 to 300 g/min or 5 to 500 g/min coal into the reactor; (2) a preheater, 20 ft long x 3/16 in diameter tubing coiled and immersed in a molten lead bath with a 20 kw electric heater to preheat the gas-coal mixture to about 425^{0}C; (3) a tubular reactor of twenty 60-ft sections of coiled tubing (3/16,1/4, 5/16 or 1/2 in diameter, depending on the investigation), of which the first two sections are immersed in molten lead and the rest in a furnace heated to reaction temperature; (4) a solid-liquid receiver; (5) condensers; (6) a filter; and (7) sampling and monitory devices.

Crushed coal is impregnated with catalyst and dried before changing in the hopper. The operating temperature of the process ranges from 475^{0}C to 566^{0}C, and the operating pressure is about 2000 psig. Solids and liquids are collected in a quenching receiver and hydrocarbons that cannot be condensed are returned to the reactor. Filtered hydrocarbon gases are recycled with hydrogen produced in the process and a supplementary cylinder of hydrogen helps maintain the operating pressure. Within the hot zone of the 1/2 in diameter reactor, residence times of coal range from 2 to 6 sec, and of gas, about 0.8 sec.

An increase in either temperature or pressure increases the conversion rate to both liquids and gases up to pressures of 2000 psi. At higher pressures, the conversion rate to liquids continues to increase slightly, but the conversion rate to gases decreases. The coal feed rate also affects the conversion rate: feed rates of 800 and 500 lb $ft^{-3}hr^{-1}$ yield 60 percent and 70 percent conversion, respectively. Oversupply of hydrogen (6 to 7

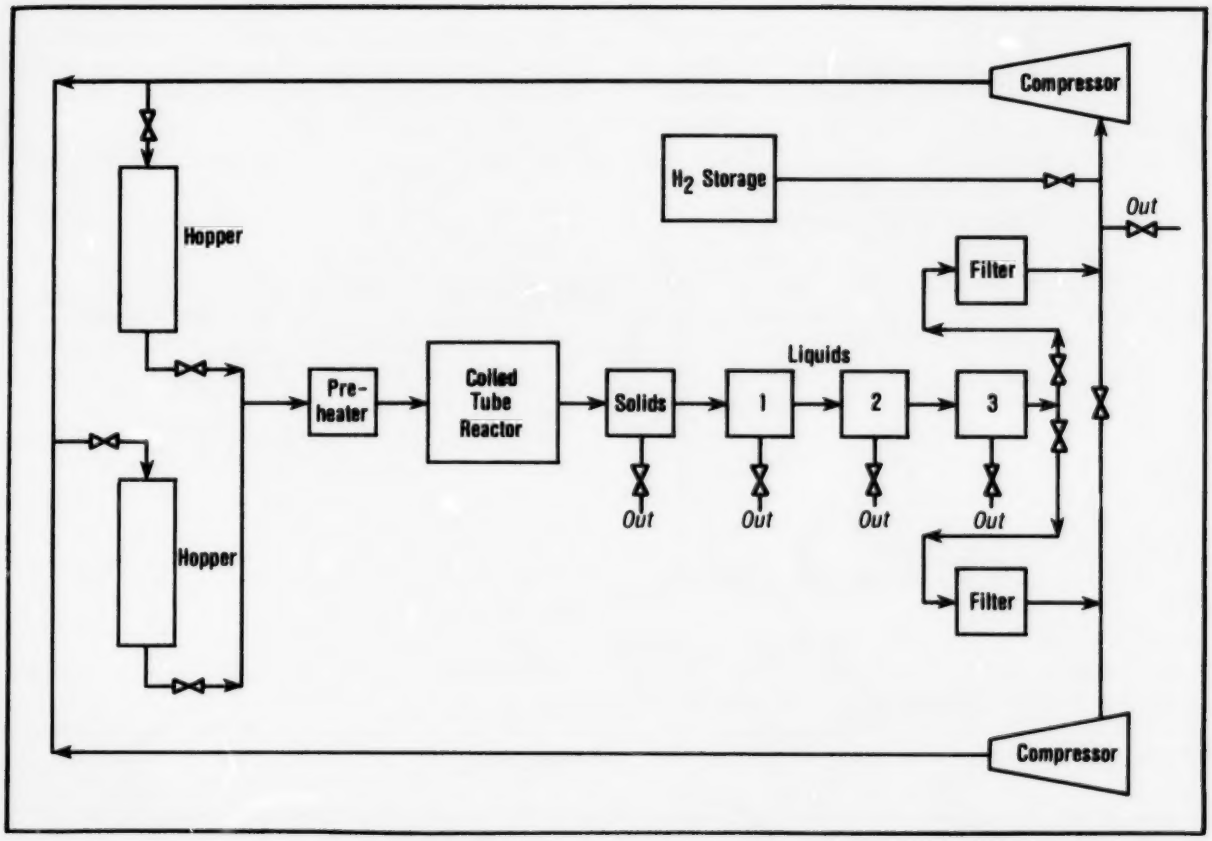

FIGURE 16. University of Utah Catalytic Hydrogenization Process PDU Flowsheet.

vol. of hydrogen to 1 vol. of coal) results in a turbulent motion which pushes the liquids out so that they fail to act as diffusion barrier. Of the product gas, 60 percent is methane and 20 percent ethane. Recycling the char generates more liquids and gases without further addition of catalyst. Reactions are exothermic: the heat produced has been estimated at about 180 Btu/lb of coal treated.

Of several catalysts tested, zinc and tin halides showed the highest activities. $ZnCl_2$ catalyst was found to be altered chemically by the hydropyrolysis reactions so that zinc could not be recovered from the reacted coal quantitatively. The difficulty of recovering the zinc appears to be inversely related to the conversion rate of the original coal; the incomplete catalyst recovery would add considerably to the total cost of the project. A study at Oakridge National Laboratory (1977) indicated that catalyst recovery costs ranged from $8.97 to $12.08 per ton of coal, based on coal value at $22.00 per ton. A catalyst loading of 3 percent Zn is adequate for reactive hvc-b or hvB-b coals but for lower rank subbituminous coals, catalyst ratios up to 8 percent are needed for effective reaction promotion.

About 18 coal samples from Utah, two lignite samples from Montana and Wyoming and one Illinois coal were tested. Some coals showed poor feeding characteristics, easily plugging the reactor. Generally, reactivities were good for hvc-b or hvB-b coals and poor for subbituminous and lignitic coals.

Below are test data from a typical run with high volatile bituminous coal from Kaiparowitz, Utah (Table 17).

TABLE 17.
Test Data from University of Utah Process

Coal analysis:	C 73.4%, H 6.0%, N 1.9%, S 0.6%
DAF-fasis	
yield, (daf-coal % basis):	
gas	16.6
light oil	14.9
heavy oil	36.6
char	35.5
water	4.4
Analysis of liquid product:	
H/C	1.21
%N	1.78
%S	0.18
flash point ^{o}C	27 - 34
pour point ^{o}C	31 - 37
asphaltenes %	15 - 22
neutral oils %	21 - 38
tar acids %	4 - 12
tar bases %	2 - 6
insoluble solids	16 - 24 (benzene insoluble)
Sp Gr. g/cc	1.070 - 1.078

PROCESS EVALUATION

Flash hydropyrolysis of coal is an extremely complex process (Howard, 1981). The number of reversible heterogeneous and homogeneous reactions and the conversion kinetics are not well understood. As discussed earlier (see section Phenomenological Chemistry), types of coal, reaction parameters and reactor geometry have immense influences on conversion mechanisms. Liquid yields depend on the hydrogen content of the feed coal, and so does the specific heat, and consequently, the heat transfer mechanism. The vitrinite component of the coal is sensitive to the rate of heating, and defines the quality of the liquid products. As a result of these various complications, most reaction models devised to correlate the carbon conversion data have been more or less empirical.

In 1979, Bechtel Corporation of San Francisco, California (Epstein, 1978), undertook to review a number of flash hydropyrolysis processes and assess them for their suitability for scale-up and their potential for economic gasification (DOE Contract ER-77-01-2565, August 1978). Processes from four institutions were evaluated; Cities Service, Rocketdyne, Pittsburgh Energy Research Center (PERC), and Brookhaven National Laboratory (BNL). Using computerized multiple-regression statistical analysis Bechtel fitted semi-empirical correlations for predicting overall carbon conversion efficiency and gaseous product selectivity to the experimental data for bituminous and subbituminous coals and lignites.

As bases for their assessment, Bechtel used the test coals described in Table 18.

The statistical analysis was used to generate a semi-empirical reaction model for correlating overall carbon conversion with the operating variables which consist of an equilibrium component, X^*, and a kinetic component, $(1-\exp(-\psi))$, satisfying a number of boundary constraints:

Carbon Conversion, $X = X^* (1-\exp(-\psi))$ where
$\psi = \alpha_1$ (gas-res. time) α_2 (part. res time) α_3 $\exp(\alpha_4$ Press.) $\exp(\alpha_5 p_{H_2})$ $\exp(\alpha_6 H/C)$ (mean particle dia.) α_7 $\exp(-\alpha_8/T_{gas})$ $(X^*)\alpha_9$
and α_i = adjustable coefficients.

The maximum reactor gas temperature (T_{gas}) was chosen as the correlating temperature variable. The predicted equilibrium carbon conversion, X^*, was estimated from a thermodynamic equilibrium computer model developed for a Propellent Evaluation Program (PEP). This model was based on a reaction system of β-Graphite, H_2, O_2, and hydrocarbon gases within the general pressure and temperature range of hydropyrolysis conditions. Carbon selectivities to gas and liquid product were obtained from the predicted values of conversion to products and the overall predicted carbon conversion:

$$\phi_{product} = X_{product}/X$$

The value of X* in the ψ function is close to unity for all of the Rocketdyne, Cities Service and BNL tests; because of this, the effect of X* on the kinetic component could not be obtained. The analysis, however, does show a strong correlation between measured and equilibrium conversion, which justifies the equilibrium hypothesis.

On the basis of these correlations, it was possible to make the following general observations:

1. for bituminous coal, overall conversion is not a statistically significant function of residence time, but the selectivity to gas is; it follows that in bituminous coal devolatilization is a very fast reaction, and liquid hydrocarbon cracks down to produce gas as residence time increases;
2. for subbituminous coal, the process is more complex; at least two steps are involved in gas generation, namely pyrolysis controlled devolatilization at short residence time and pressure-controlled hydrogenation of reactive char at longer residence time; overall carbon conversion is a significant function of particle residence time, gas temperature, and pressure; with long particle residence times, higher conversion needs higher hydrogen partial pressure, with short particle residence time, conversion decreases with increasing partial pressure of hydrogen;
3. methane production increases with temperature and particle residence time for both types of coal;
4. the equilibrium model predicts that a reactor system producing significant quantities of hydrocarbons higher than C_2 would operate in a kinetically controlled regime far removed from equilibrium;
5. in entrained flow processes, particle residence time is equal to gas residence time but in free-fall processes, it is less than gas residence time;
6. under comparable operating conditions, the Cities Service bench-scale reactor and the Rocketdyne 0.25 ton reactor would exhibit similar carbon conversion and selectivity to gas from subbituminous coals;
7. because of hydrogen to coal ratios (0.2 to 2 lb/lb) used in Cities Service, Rocketdyne and BNL reactors, data were generated in a kinetic-controlling regime; PERC test data on the other hand, were generated in a thermodynamic equilibrium between the carbon in coal and the reaction products; hydrogen-to-coal ratios were low (0.03 to 0.12 lb/lb), and equilibrium conversion was 40 to 65 percent with lignite and 15 to 35 percent with bituminous coals; methane was the major product in both cases.

TABLE 18.
Typical Analyses of Coals Tested in Reactor Systems
(Cities Service, Rocketdyne, BNL and PERC)

Analysis	North Dakota Lignite	Montana Rosebud	Kentucky #9/14 Colonial	Kentucky #9 Hamilton 2	Illinois #6 Orient 3	Pittsburgh Bruceton
moisture wt %	7.8	5.6	1.9	5.0	6.8	1.2
ash wt%	5.6	10.0	10.8	9.2	9.3	5.7
V.M. wt%	39.7	36.3	36.9	36.5	33.6	36.4
H/C	0.800	0.846	0.837	0.817	0.793	0.783
rank % C daf	68.2	72.5	78.4	81.8	82.0	84.0
N wt % dry	1.2	1.1	1.5	0.9	1.0	1.6
S wt % dry	1.4	1.0	4.3	2.8	1.8	1.1

TABLE 19.
Test Data from the Cities Service-SRT Process (March 1979)

Coal	N. Dakota Indian Head	Texas PSOC-412	Montana Decker	Iowa Big Ben	W. Kentucky Beulah	Utah Hiawatha
coal-analysis daf %						
C	68.4	67.4	72.5	75.3	78.4	79.2
H	4.6	4.7	5.3	4.9	5.5	5.9
N	1.3	1.9	1.6	1.6	1.7	2.4
S	0.8	2.0	0.5	2.6	6.5	0.6
% carbon-conversion	52.1	62.7	39.4	68.8	32.7	46.6
% carbon selectivity to liquid	45.3	28.7	37.6	38.1	50.4	26.1

The reactor model proposed by Bechtel Corporation was designed to determine the suitability of flash hydropyrolysis processes for gas production; to assess processes as to their potential for liquid production it needs some modifications. For optimized liquid production, the hydropyrolysis process has to be operated in the kinetically controlled regime, where the numerical values of the Bechtel model's variables are different from thermodynamic-equilibrium values. Partially devolatilized coal may not have the same thermodynamic properties as β - graphite. Increased gas yields from a given coal are believed to arise from secondary cracking of primary liquid products and from hydrogenation of leftover char or carbon. In order to prevent such secondary reactions, particle-heating time has to be shortened by efficient mixing of the hot hydrogen with the powdered coal and the products have to be quenched as quickly as possible.

In recent tests, Cities Service partially achieved such conditions in their helical entrained downflow reactor equipped with a Rocketdyne, water-cooled, 4-in-1, coal/hydrogen injector system. Under standardized conditions (reactor temperature 725°C, pressure 2200 psi, vapor residence time 3000 msec, gas velocity 20 ft/sec, hydrogen/coal ratio (2 to 4 lb/lb), six different coals were processed to yield liquids and gases. The percent carbon selectivity to liquid (defined as percent carbon converted to liquid product/ percent total carbon conversion) varies from 25 to 50 percent depending on the type and nature of the coal (Table 19).

Although the North Dakota and Texas lignites belong to the same rank, the former produced a larger oil yield than the latter. The high sulfur content in the Texas lignite, however, could not have been the factor inhibiting oil formation, since west Kentucky No. 9 coal has equally high sulfur content and high selectivity for liquid yields.

On the other hand, one can find a valid correlation between maceral composition of the test coals and carbon-selectivities to liquid products (see Table 20). Except for west Kentucky high-sulfur coal, the higher the exinite content the higher the liquid yield under SRT process.

Cross-correlation of all the available hydrocarbonization or flash-pyrolysis data is difficult because different investigators have employed different types of reactor systems as dictated by individual interest. A well-defined coal has not been tested under standardized conditions in different reactor systems. It is seldom possible, therefore, to compare the performance of one reactor system with that of another, especially under a variety of

TABLE 20.
Maceral Compositions and Carbon Selectivity to Liquid-yield

Coal	N. Dakota lignite	W. Kentucky	Utah	Montana
maceral content				
vitrinite %	58.3	67.1	61.2	60.0
exinite %	16.9	5.3	10.9	9.1
fusinite %	9.1	3.1	3.3	8.7
liquid-yield*	23.6	16.5	12.2	14.8

*% carbon converted to liquid

TABLE 21.
Typical Fischer Assay (500°C) Data of American Coals
(as received basis)

Rank	Coke %	Tar %	Water %	Gas %	Error
lvb	89	3.2	3.2	4.6	+1.6
mvb	83	7.2	4.1	5.7	+2.5
hvAb	75	11.7	6.0	7.3	+3.0
hvBb	70	11.0	11.0	8.0	+2.2
hbCb	67	10.2	15.9	7.1	+3.3
sub-A	59	7.8	-	-	+1.2
Sub-B	57	5.8	27.8	9.4	+1.0
lignite	36	5.4	50.0	4.2	+3.4

feed coals. From the chemistry of the process and the types of coal used, however, it is possible to make some educated guesses predicting the performance of a particular reactor system using a particular coal.

Typical pyrolysis assay data, based on about 200 different coal samples from U.S. deposits are shown in Table 21. These data demonstrate the connection between elemental composition and tar yield. They also reveal that during thermal decomposition of coal, both oxygen and carbon compete for hydrogen to generate tar, water and gas.

With higher coal ranks (lower O/C ratios), pyrolysis yields of liquids (tar and light oil) are progressively greater up to carbon content 87 percent, but are less beyond that limit. There is a threshold hydrogen content below which tar is not produced by thermal decomposition of coal.

In Table 22, Fischer assay data of different coals are compared with the process yield data. It appears that conversion to liquid and gaseous products can surpass Fischer assay values if the coal is subjected to hydrocarbonization processes. Temperature, pressure and residence time are the distinguishable variables governing product-yield. Maximum oil yield, while depending to some extent on the hydrogen content of the feed coal, is achieved with temperatures in the 450 to 600°C range. But the gas yield increases continually with temperature, so that at very high temperatures (1200°C), hydrocarbon gases are the principal products.

Most of the available experimental data are grouped in two pressure ranges: below 1500 psi, and from 5000 to 6000 psi. Intermediate data have not yet been adequately studied. Both oil and gas

production from all coals tested increase with partial pressure of hydrogen although there is an absolute difference in yields between bituminous and subbituminous coal. Oil yields appear to increase as the square root of pressure, leveling off at about 6000 psi.

The particle residence time is a significant factor in processing subbituminous coal and in carbon-gasification to produce methane.

The Alberta coals classified as sub-A and hvc-b are comparable to the Kentucky, Montana, Wyodak and Wyoming coals tested in the TOSCOAL, SRT-Rocketdyne and Occidental (Garrett) processes (see Table 22). They would be expected to produce about one-and-one-half times the Fischer assay liquid yield by any one of these processes. Liquid product from these Alberta coals, using the Occidental (Garrett) process, would chiefly consist of heavy tar which would need hydrorefining. On the other hand, the SRT-Rocketdyne process would produce chiefly hydrocarbon gas and BTX-products. Since the amount of heavy components in the liquid-product can be minimized, the cost of hydrorefining could also be reduced following Rocketdyne process concepts.

CATALYTIC HYDROCARBONIZATION

Test results from University of Utah and Cities Service investigations demonstrated that zinc and stannous chloride catalysts effectively increase the liquid yield in coal pyrolysis under short-residence-time conditions. This increase is more pronounced with bituminous than with subbituminous coals giving 20 to 53 percent increase

TABLE 22.
Comparative Data of Fischer Assay and Flash-pyrolysis Process Yield

Source	COAL % C	% H	ASSAY DATA* Tar	Gas	PROCESS DATA* Tar	Gas	PROCESS
N. Dakota	68.2	4.5	11.5	-	27.6	-	Cities Service/Rocketdyne
Wyodak, Wyoming	71.5	4.3	19.1	16.5	20.1	13.6	TOSCOAL
Europe	71.6	5.4	15.3	18.6	27.5	16.8	Lurgi-Ruhrgas
Montana	72.5	5.1	-	-	16.8	28.6	SRT-Cities Service
Wyoming	76.4	4.8	14.8	17.3	22.2	16.1	Occidental (Garrett)
Kentucky #9	78.4	5.5	21.3	6.2	18.8	36.4	SRT-Rocketdyne
Pittsburgh #8	80.0	5.5	23.5	6.9	39.4	30.0	COALCON
Kentucky #11	80.3	5.5	22.2	6.8	47.6	8.9	Occidental (Garrett)
Utah	79.2	5.5	25.2	6.9	14.3	14.0	SRT-Cities Service
Kentucky #14	81.8	5.5	23.5	4.8	14.4	66.1	SRT-Rocketdyne
Illinois #6	79.2	5.4	15.6	7.4	29.7	19.2	COED
Illinois #6	82.0	5.5	16.4	7.5	25.1	37.0	SRT-Rocketdyne
Pittsburgh #4	84.0	5.5	19.8	6.2	11.6	26.6	SRT-Rocketdyne
New Mexico	84.5	6.0	21.9	4.0	55.0	37.3	Schroeder
*Expressed as g per 100 g feed-carbon.							
Comparable Coal From Alberta							
Edmonton	72.0	4.9	14.0	24.8	?	?	?
Drumheller	76.4	5.1	14.3	16.1	?	?	?
Prairie Creek	79.8	5.2	17.3	11.1	?	?	?

in carbon conversion in the case of the former and 7 to 13 percent in the case of the latter.

The pronounced effect of zinc chloride may be explained by the fact that it is a Lewis acid, in the liquid phase at the reaction temperature. "Proto-bitumen," released at the fast-heating rate, would come into direct contact with the Lewis acid and undergo a cracking reaction. The lessened effect of the catalyst on conversion of subbituminous coals is caused by their higher oxygen content, which inhibits the reaction. Zinc chloride here should act to facilitate acid-catalyzed condensation reactions of the oxygenated compound so that less "proto-bitumen" would be released for cracking.

An ammonium molybdate catalyst showed negative effects in the University of Utah and Cities Service tests, but in Schroeder's process, gave the best positive result. Possibly the process chemistry of Schroeder's process is entirely different. Molybdate-catalyzed gas phase hydrogenation of the evolved tar, coupled with short residence time and efficient heat-transfer, yields abundant products from the perhydrous, high volatile bituminous coals tested. The Occidental (Garrett) process with downstream refining of the liquid, however, should produce identical yields from the same coals.

Some difficulties are experienced in the catalytic hydrocarbonization. For one thing, the effect of catalysts diminishes quickly when temperatures are raised beyond 600°C. Furthermore, when zinc chloride is used as the catalyst, zinc may be quite difficult to remove from the char depending on the extent of conversion. Recovering 99 percent of the catalyst adds considerably to the cost of the process, as much as $8.97 to $12.07 per ton of coal at $22.00 per ton in a 25 000 ton/day plant.

THE PROPERTIES OF LIQUID PRODUCTS

The quality of crude liquids produced by flash-pyrolysis or hydrocarbonization processes does not depend on the types of feed coals but on the process itself. In general, flash-pyrolysis tars are much heavier than hydrocarbonization tars, which tend to be less viscous oil. Some typical analytical data are shown in Table 23. COED, Occidental (Garrett), Lurgi-Ruhrgas, and TOSCOAL processes are based on similar process chemistry, yet the crude liquids from the Occidental (Garrett) process have less hydrogen and are more viscous than the liquids obtained from the other processes. From SRT processes, where hot hydrogen is intimately mixed with evolving tar, the H/C ratio of the liquid product from almost any type of coal is close to

TABLE 23.
Properties of liquid products (crude) obtained from Flash-Pyrolysis Process

Rank of Feed % C	Process	H/C	Density g/cc	Distilled vol%	Distilled °C	Asphaltene wt%
79.2	COED	1.00	1.090	64	562	-
62.4	Garrett	0.66	1.120	-	-	45.0
	Lurgi-Ruhrgas	1.00	1.168	90	318	-
68.2	SRT-Rocketdyne	0.95	1.013	90	334	0.6
72.5	SRT-Rocketdyne	0.92	1.013	90	361	3.6
	SRT-Rocketdyne	0.91	-	90	363	0.3
78.4	SRT-Rocketdyne	0.88	-	90	378	9.6
82.0	SRT-Rocketdyne	0.90	-	90	331	0.5
71.5	TOSCOAL	1.28	1.036	50	385	-
80.6	U of Utah	1.18	1.073	-	-	15.7

unity and reaction conditions can conceivably be varied to favor production of BTX. Similarly, in catalytic processes, the properties of liquid products can be adjusted by changing the reaction conditions.

The nitrogen content of coal liquids always corresponds to that of the feed coal, while the sulfur content never exceeds 0.5 percent.

The aromaticity of the crude pyrolysis liquids is highest from flash-pyrolysis processes, considerably lower from hydrocarbonization processes and lowest from catalytic hydroprocessing.

In general, differences in coal pyrolysis product composition and properties arise from the secondary reactions that evolved tar undergoes in the reactor of a specific process under specific conditions.

ENGINEERING VIEWPOINT

The chemistry and experimental results relating to coal pyrolysis have been covered in the preceding sections. In this section, factors relevant to design and operation of a commercial installation will be considered in the light of the current state of development of pyrolysis technology. The factors to be considered fall into four major categories:

1. conversion concept;
2. design plant;
3. process operation;
4. development status.

Conversion Concept

The major product of all coal pyrolysis routes is residual solid char or coke and the economics of pyrolysis-based processes depend upon disposition of this solid. Efforts have been made, however, to minimize the yield of residual solids and these have followed three routes:

a. staging the pyrolysis reaction to take advantage of the decreased caking tendency of partially devolatilized coal; this approach is the basis of the COED process;
b. pyrolyzing the coal rapidly with removal of pyrolysis products as they are formed to minimize polymerization and continued cracking (for example, Lurgi-Ruhrgas and Occidental);
c. pyrolyzing the coal in the presence of hydrogen to stabilize the initial products of pyrolysis; these are the hydropyrolysis and flash hydropyrolysis processes.

These have all been described earlier.

The uses considered for the by-product char from pyrolysis processing are:

1. fuel for direct combustion;
2. feedstock for gasification to yield fuel gas;
3. feedstock for hydrogen production.

The first two could yield by-product electric power for plant use and for sale while hydrogen from char would be used in upgrading coal liquids.

The liquids generated require additional processing before use, being in general a mixture of light and heavy oils with pitch, co-condensed water and entrained solids from the pyrolysis routes and light oil, water and solids from hydropyrolysis routes. The liquid product from subbituminous coal feed has high nitrogen and oxygen contents and sulfur proportional to the coal being pyrolyzed.

The "downstream" use of the char must also be of concern since its utilization is an integral part of the overall conversion scheme. The char will retain all of the ash components of the original coal and a portion of the sulfur. Trace constituents of the coal will normally be concentrated in the char. In the pyrolysis process, the coal releases some of its volatile component and, because of the loss of water and hydrocarbon, the char has a higher carbon content than the original coal.

These reactions have the following consequences on char utilization. The loss of volatile components, if carried sufficiently far (15 percent $>$VM) can

cause the char to be difficult to burn in a conventional boiler because of poor ignition characteristics. This necessitates use of special equipment such as fluidized-bed boilers or the use of a supplementary fuel for firing. The higher carbon content of the fuel and resulting higher combustion temperatures can cause higher NO_x emissions upon combustion (although fluidized-bed combustion would counteract this). In addition, the increased ash concentration may cause excessive particulate emissions on combustion. The sulfur content of the char will normally be lower than the parent coal but could be higher under some conditions with consequent SO_2 emission upon combustion.

Plant Design

a. Reactor Type: The pyrolysis processes described above all depend upon the rapid transfer of heat to the coal which is normally ground to improve the transport rate. The reactors for these processes are generally of the entrained or fluidized-bed types to assist the transfers. Entrained reactors are capable of handling any coal type but depend upon the transfer of heat by the hydrogen stream entraining the coal. In the case of fluidized bed pyrolysis, coking or caking coals must be pretreated to eliminate the caking tendency. Heat transfer takes place either through the wall of the fluidized-bed reactor using combustion of pyrolysis gases as the heat source or by injecting flue gas from combustion of pyrolysis gas as fluidizing gas.

b. Coal Feeding: Coal feeding is a difficult function to carry out, especially in the hydropyrolysis routes that operate under pressure. Existing methods involve auger feeders or lock hoppers for low pressure operation and lock hoppers or slurry injection for higher pressures (none of the pyrolysis routes at present use slurry injection). Difficulties with coal feed systems involve both component wear due to abrasion (for example, the seats in lock hoppers) and the difficulty in minimizing thermal decomposition of the coal exterior to the reactor. The former problem is minimized by using replaceable wear plates on the lock hoppers; the latter problem is eliminated to a great extent by water cooling of the injector. In an effort to improve coal feeding to high pressure reactors, the U.S. Department of Energy has been funding development of extrusion feeders for dry feeding coal. These feeders are not ready for industrial use; nevertheless, they would not be suitable for injecting particulates. The extruded coal spalls off in chunks when pressure is released as it enters the reactor, but these chunks would not have a sufficiently high surface area to be reactive unless a grinder was installed within the reactor to reprocess the extruded coal.

c. Materials of Construction: While the service is admitted to be severe, the pyrolysis processes do not pose any unexpected problems because of the experience already gained through pyrolysis of caking coals for solid coke and by-product liquids. Vessels would normally have insulation included inside the reactor so that the outer reactor wall could be held at lower temperatures. The products of pyrolysis, such as tar acids, and hydrocarbons, are not excessively corrosive. Some refractories are decomposed when in contact with hydrogen at high temperature, for instance:

$$H_2 + SiO_2 \Rightarrow SiO + H_2O.$$

In addition, the shells used for hydropyrolysis reactors must be protected from hydrogen embrittlement through shielding with impermeable insulation or through selection of a suitable steel for the shell. Pumps and valves are also subject to erosion. Outflow dischargers suffer from the same corrosive conditions as do input feeders. Recovery will be made by auger or lock hopper for atmospheric reactors and by lock hoppers for pressurized reactor systems. Pressure let-down valves are subject to particularly severe erosion in the case of pressurized operation.

Process Operation

Of concern in process operation is the operability of the process (for example, the degree of control

available through varying reaction conditions) and the environmental considerations associated with the process. Pyrolysis processes do possess some flexibility as the yields are a fairly strong function of the time-temperature history of this reaction. In general, solid yield decreases with increasing temperature, gas yield increases with increasing temperature and liquid products yield increases initially and then decreases with increasing temperature.

Pyrolysis of coal (by any process) generates polycyclic aromatic molecules which may be dangerous to the health of personnel. Care must be taken to shield employees and the public from potentially dangerous contacts with chemicals generated by the processes. While this is an area of concern, it is not a cause for alarm as the chemicals generated are no different in type than those that have been produced for decades by the pyrolysis of coal for coke manufacture. Here there have been relatively few harmful effects noted, largely because of the care taken by the industry.

Development Status

The only pyrolysis route noted above which has been commercially applied and is available commercially is the Lurgi-Ruhrgas process which is used for lignite pyrolysis at one plant in Yugoslavia and for pyrolysis of bituminous coal in England. The Yugoslavian plant produces granular char for use in coke manufacture while the English plant produces carbon for formcoke production. The COED process has been operated in a 36 ton/day pilot plant for extended periods and is likely capable of satisfactory scale-up. Rapid hydropyrolysis has been operated at the one ton/hr level by Rockwell International although only for brief test periods. The Occidental (Garrett) process has been tested in a 3.6 ton/day process development unit. Hydropyrolysis of coal in a fluidized-bed reactor has been tested in pilot plants ranging to 1500 lb/hr by Union Carbide. Plans were underway to construct and operate a demonstration plant under the name COALCON process. Work was discontinued because of concerns about the operability of the process with caking eastern coal and about the economics of the process.

ALBERTA SCENE: APPLICABILITY OF PYROLYTIC PROCESSES

Establishing new technology at a specific location depends on a multitude of economic, political, social, and technological factors. In this section the scope of discussion will be limited to technological factors only. Under the current state of development of pyrolysis technology, evaluation of processes will be based on the products they will generate.

LIQUID, GASES, AND CHEMICALS AS PRIMARY PRODUCTS

A comprehensive energy and resource management policy for Alberta should aim to maintain the current pattern of coal resource utilization at least up to the turn of this century. Subbituminous coals would continue to meet the domestic demand for power generation and bituminous coals would remain dedicated for export markets. In this context, a research and development program towards pyrolysis in Alberta can have only limited objectives. There are genuine prospects for the extraction of volatile components from the coal for chemical feed stock and refinery additives, but production of high Btu gas and transportable fuels by pyrolysis has little commercial potential.

From the chemical standpoint, catalytic hydrocarbonization processes seem poorly adapted to the subbituminous coals of the province. Economic suitability also seems wanting. McConaghy (1978) made a preliminary cost estimation of Schroeder's catalytic process. McConaghy assumed that this process could produce 70 percent of feed weight as liquids (an assumption which needs verification), and estimated that liquid products from Alberta coal would cost in the range of $25.00 to $30.00 per bbl in 1978 dollars.

Hydrogen as Primary Product

The increasing demand for hydrogen in the energy technology of the province opens up the prospect of utilizing Alberta coals for hydrogen production. Research and development for this purpose can be based on Occidental (Garrett), Lurgi-Ruhrgas or TOSCOAL processes, but selection of the specific process will depend on char reactivity. There is a need for research on the reactivity of char from Alberta subbituminous coals as it relates to both gasification and combustion. Gasification of these coals to methane by the Cities Service-Rockwell's SRT process seems to be impractical at the present time, but partial conversion by SRT process and utilization of the char for hydrogen production is worth considering. Test runs of Alberta coals now in progress in the Cities Service pilot plant with this objective in mind may generate useful data towards further research and development.

LIQUIDS AND GASES AS BY-PRODUCTS FROM THERMAL POWER PLANTS

By comparing the assay characteristics of American coals with those of Alberta subbituminous coals, either flash pyrolysis or catalytic hydrocarbonization would yield about 1 bbl/ton refinable liquids and/or 4000 scf/ton medium-Btu gas from the latter at optimum efficiency. It would be justifiable to add a pyrolysis unit on the front of a major thermoelectric generator complex to extract the volatiles from the feed as a high value by-product. Pilot-plant data presented in the foregoing review may be used to evaluate the available processes for such an installation and to initiate a detailed engineering design.

McConaghy (1977) estimated the cost of Alberta COED-synthetic crude in Alberta at $26.68 per bbl from a 118 900 bbl/day facility, assuming 10 percent interest rate and 15 percent discounted cash flow rate of return. Herring (1979) submitted an economic appraisal of the Lurgi-Ruhrgas process installed on the front end of three 376 Mw power generation units proposed for Keephills, Alberta, to extract synthetic crude from Keephills coal. He estimated the capital cost for the added plant at $380 million to produce 14 844 bbl/day of low sulfur aromatic synthetic crude. With coal valued at $4.54 per ton and product liquid at $16.47 per bbl in 1980 dollars, the project would earn a discounted cash flow rate of return at 17.4 percent after tax and pay out in 7.1 years. Both these economic studies assumed carbon selectivities for liquid yields comparable to those from hvB-b coal so that cost figures are somewhat lower than should be budgeted for.

Full evaluation of the potential of producing marketable by-products from thermoelectric plants will require extensive testing to select the most suitable process routines, to optimize product slates, and to determine product qualities and char reactivities for site-specific coals.

INFERENCES AND RECOMMENDATIONS

The kinetics and mechanism of coal pyrolysis are very complex. Devolatilization and decomposition processes comprise a series of sequential partly overlapping reactions which have important bearing on research and development activities based on pyrolysis. Yields and product composition are critically dependent on coal type and operating conditions. Most of the available test data stem from operating high volatile bituminous coals which produce high liquid yield. To date subbituminous coals have received little attention (except for development work related to SNG-generation from coal); as a consequence, reliable prediction of product yield and compositions from these coals is a difficult task at the present level of understanding of the processes.

The pyrolytic properties (as defined from the assay data) of Alberta subbituminous coals showed wide variation. Tar and light oil yields can vary from 4 to 13 percent for samples within the same deposit. Liquid yield from this type of coal generally corresponds to assay yield when flash pyrolysis mode is applied. However, it is claimed that under hydropyrolysis conditions, Cities Service-Rocketdyne process conversion may exceed assay results. In order to develop a viable technology, extensive research and development will be required.

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